Sorption and Desorption Processes of Organic Contaminants on Carbonaceous Materials

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List of abbreviations

C	Concentration [mg/l]
C_{OC}	Concentration of the compound in organic carbon [mg/kg]
C_{OM}	Concentration of the compound in the organic matter [mg/kg]
CM	Carbonaceous material
C_S	Concentration of the compound in the solid phase [mg/kg]
$C_{S,0}$	Maximum concentration on the solid phase at full surface coverage [mg/kg]
C_w	Concentration of the compound in the liquid phase [mg/l]
D_a	Apparent diffusion coefficient [cm²/sec]
E	Characteristic free energy of adsorption of a compound [KJ/mol]
f_{OC}	Fraction of organic carbon in the soil or sediment [-]
K_d	Linear distribution coefficient [l/kg]
K_{Fr}	*Freundlich* sorption coefficient [L/kg]
K_L	Langmuir sorption coefficient
K_{OC}	Octanol/water coefficient
K_{OW}	Coefficient of a hydrophobic compound
N	*Freundlich* exponent [-]
R	Ideal gas constant [J/mol/K]
S	Compounds solubility [mg/L]
T	Temperature [K]
V_0	Maximum volume of sorbed chemical per unit mass of sorbent [cm^3/kg]
V_{om}	Molar volume of the organic phase [L/mol]
ρ_0	Compounds density [g/cm^3]
ρ_{OM}	Density of the organic matter [kg/cm³]
γ_{OM}	Activity coefficient [-]

To whom whoever Inspired Me……..

To whom whoever in My Heart……

To My Beloved Late Father

I dedicate this work

Engy

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Abstract

Sorption is considered the most important abiotic process for determining the fate and transport of organic contaminants in the environment. Hence, we investigated whether sorption is fully reversible or whether a irreversibly sorbed pollutant fraction remains in the sorbent and if the total amount of contaminants is available to biological receptors or only a fraction of them. This process has a great importance for remediation targets. This question was examined in multi-stage batch sorption and desorption experiments with Trichloroethylene (TCE) and Tetrachloroethylene (also perchloroethylene PCE), as well as o-xylene and p-xylene, in combination with the sorbents activated carbon, charcoal, peat, and the hydrophobic zeolite Y-200. It was shown that the structural composition of the sorbent is one of the important features for a contaminant adsorption-resistant fraction. Hence, the rigid pore system of micro porous zeolite Y-200 exhibits the mostly reversible sorption. Charcoal and activated carbon showed a significantly irreversible sorption, or at least a very slowly desorbing pollutant fraction. This fraction can be harmful in environment due to different kinds of pollutants. Competitive sorption may cause releasing of this fraction.

Generally, the results indicate that the sorption in the above mentioned sorbents for the different chemicals investigated is dominated by pore filling processes, except for peat. A nonlinear type sorption isotherm is described by the combination of the partitioning and pore-filling mechanisms.

Abstrakt

Sorption wird als der wichtigste abiotische Prozess zur Untersuchung des Transports und Verbleibs von organischen Schadstoffen in der Umwelt angesehen. Für die Wasseraufbereitung ist es von großer Bedeutung, ob die Sorption vollständig reversibel ist, ein Teil der sorbierten Schadstoffe irreversibel im Sorbens verbleibt und ob die Gesamtmenge oder nur ein Teil der Schadstoffe für biologische Rezeptoren verfügbar ist.

Im Rahmen der Arbeit wurde diesen Fragestellungen in mehrstufigen Sorptions- und Desorptionsversuchsreihen nachgegangen. Als Sorbentien kamen Aktivkohle, Holzkohle, Torf und hydrophober Zeolith Y-200 zum Einsatz, welche den Modellverbindungen Trichlorethylen (TCE), Tetrachlorethylen, Perchlorethylen (PCE), o-Xylol sowie p-Xylol ausgesetzt wurden.

Es wurde gezeigt, dass der strukturelle Aufbau des Sorbens maßgeblich für das Sorptionsverhalten der Verunreinigungen ist. Das starre Porensystem des mikroporösen Zeoliths Y-200 wies bezüglich der Sorption den höchsten Reversibilitätsgrad auf. Holz- und Aktivkohle zeigten eine signifikant irreversible Sorption bzw. ein zumindest sehr langsames Desorbieren der Schadstoffe. Da die verbliebenen Schadstoffe durch kompetitive Sorption anderer Verunreinigungen im Wasser wieder freigesetzt werden können, stellen sie eine potentielle Umweltgefährdung dar.

Allgemein gilt, dass die Sorption der untersuchten Chemikalien in den oben genannten Sorbentien mit Ausnahme von Torf durch porenfüllende Prozesse dominiert wird. Die theoretische Beschreibung der Sorption gelang durch nichtlineare Sorptionsisothermen, die mechanistisch gesehen sowohl Verteilungsgleichgewichte als auch Porenfüllung umfassen.

1. INTRODUCTION

The extensive production and release of volatile organic compounds (VOCs) has led to a widespread contamination of soils and sediments with these pollutants throughout the world, threatening drinking water resources. Especially halogenated hydrocarbon compounds (HHCs) such as trichloroethene (TCE) and perchloroethene (PCE), used mainly in dry cleaning and metal degreasing processes, and petroleum hydrocarbons as constituents of gasoline such as benzene, ethylbenzene, toluene and the xylene isomers (BTEX), are among the most frequently detected groundwater contaminants (NRC, 1994).

In addition, the heterogeneity of aquifer systems and the large number of abiotic and biotic transformation processes can lead to complex migration and degradation patterns of contaminant plumes (Fig. 1). Various methods have been developed and tremendous amounts of money have been spent to remediate such contaminated sites. However, in many cases remediation efforts have not been successful in an acceptable time frame due to various reasons. One main reason is the complexity of sorption processes of the contaminants on natural organic matter in the subsurface with mass transfer limitations causing extremely long remediation times. Although a lot of research efforts have been invested to get a fundamental understanding of the complex problems, there are still open questions that have to be addressed.

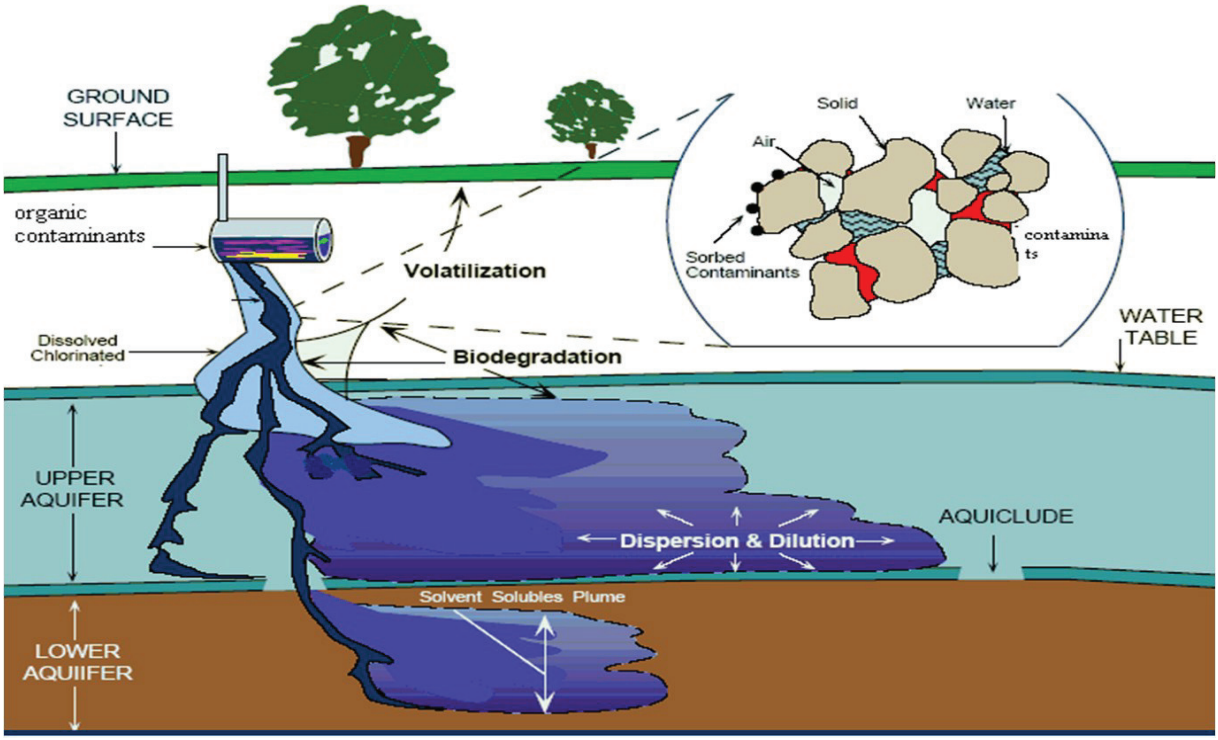


Fig. 1: Typical scenarios organic contaminants in the ground water [(1)].

1.1 Motivation

Sorption of organic contaminants on carbonaceous particles in soils and sediments is the most important abiotic process that governs the mobility of contaminants in the subsurface. Assuming a high affinity of the contaminant to the soil organic matter, transport processes are strongly retarded and the contaminants accumulate in the soild phase. Is the source of the contamination depleted, or if remediation measures are implemented, contaminant concentrations in the aqueous phase decrease resulting in a desorption of contaminants. This desorption is often diffusion limited resulting in very long remediation times.

These processes are quite well understood; they are modeled and are implemented into reactive transport models (Ball & Roberts 1991a[1]; Grathwohl, 1998; Allen-King et al. 2002). However, there is a controversal discussion whether sorption processes are fully reversible or whether hysteresis is occurring during desorption resulting in an irreversibly sorbed contaminant fraction (e.g. Huang et al. 1998; Braida et al. 2003; Ran et al. 2003). This fraction would remain in the sediments and could not be removed *via* the aqueous phase using hydraulic remediation measures. This is of high relevance, for example in defining remediation targets for contaminant concentrations in soils.

Various models have been developed to explain desorption resistant contaminant fractions, i.e. pore deformation processes (Kan et. al, 1997; Lu & Pignatello, 2002), in which sorbed molecules cause an widening of pores. This process was also described by Braida et al. (2003), who postulated that sorption of benzene on activated carbon results in an expansion of the sorbent. During desorption, the opposite effect occurs and molecules are trapped in the sorbent and are unable to desorb. However, they observed a decrease in hysteresis with an increase in concentration, although the opposite effect would be expected. Jonker & Koelmans (2002) explained the different effectiveness of solvents for the extraction of plycyclic aromatic hydrocarbons (PAH) also with an expansion of the sorbent.

Also different experimental concepts were proposed to enable the investigation of an irreversible sorbed contaminant faction. In most cases sorption experiments are performed that are followed by desorption experiments. Based on mass balance considerations an irreversible sorbed contaminant fraction is calculated. Main problem of this approach is, that desorbing contaminants have to be precisely quantified over long time periods. This is especially complicated in the late stages of desorption when very low desorbing masses have to be quantified. The evaluation of potentially irreversible sorbed contaminant fractions is then prone to large errors and experimental artefacts can lead to significant errors (Huang et al. 1997).

To minimize experimental artefacts resulting from repeated opening and closing of reaction vials, sorption and desorption processes have been initiated by changes in temperature only. Wang et al. (2007) did not find hysteresis for the desorption of phenanthren from different carbonaceous sorbents. Sander & Pignatello (2005)

performed sorption and equilibration experiments with naphthalene and C-14 labelled naphthalene and concluded that deformation processes of the organic matter play only a minor role for desorption hysteresis.

Here a simple experimental approach is presented that is suitable for an investigation and quantification of desorption hysteresis. For this, multi-step sorption- and desorption experiments were performed with pairs of similar organic contaminants. By using different sorbents a potential sorption hysteresis can be related to the physical properties of the sorbents.

2. THEORETICAL BACKGROUND

2.1 Introduction

The release of volatile organic compounds (VOC) into the environment is a serious problem as they distribute between the different phases in natural systems (solid phases, liquid phases, vapour phases). Sediments can be considered as a sink for VOC's because of their hydrophobic nature and the resulting affinity to the sediment's organic matter. Consequently, sorption/desorption processes are the most important factors that determine the fate of VOC's in the environment.

Slow desorption kinetics was found to be the major cause of very long times that are often required for remediation of contaminated soils and sediments. Slow desorption also limits the bioavailability of VOC's that potentially can be degraded by biological processes (Rockne et al., 2002). However, there is still a controversial debate in the scientific literature whether sorption processes are fully reversible or whether there is some fraction that is sorbed irreversibly. The existence of such a fraction would limit remediation efforts and would also have implications for the definition of treatment goals during remediation efforts.

There are several factors that control desorption processes and the relative extent of desorption such as swelling of the sediment organic matter, the characteristics of mineral surfaces, or the micropore size in the geosorbents. (Johnson et al., 2003; Li and Werth, 2004; Chen and Xing, 2005; Cheng and Reinhard, 2006; Xu et al., 2006; Ran et al., 2007; Shih, 2007). The reasons for the sometimes observed desorption hysteresis are not yet fully understood. However, it was proposed that sorption of the sorbate molecules may cause deformation of flexible sorbent solids, such as natural organic matter and organo-clays resulting in an entrapment of sorbed molecules during desorption (Weber et al., 2002; Lu and Pignatello, 2004).

It was suggested that desorption consists of three stages which are fast, slow, and very slow (Cornelissen et al., 2000; Cornelissen et al., 2001). Several researchers have tried to associate the maximum sorption capacities of organic compounds with the sorbed amounts in the slow and very slow desorbing domains (Van Heuvel et al., 2005; Van Heuvel and Van Noort, 2005). These researchers proposed that the fraction of compounds existing in the rapidly desorbing domain were sorbed by partitioning, and the fractions trapped in the slow and very slow desorbing domains were sorbed by pore filling.

Organic matter consists of soft carbon, where portioning is the main sorption process and hard carbon, where pore filling mechanisms dominate (Zhao et al., 2002; Chai et al., 2007). The authors found that the values for hole filling adsorption capacities of organic compounds in two soils and one sediment were almost equal to the sum of the amounts sorbed in the slowly and very slowly desorbing domain.

2.2 Sorption

Sorption of hydrophobic compounds to natural solids has been intensely studied over the last decades (Karikhoff et al., 1979; Grathwohl, 1989; Ball and Roberts, 1991a,b; Poerschman and Kopinke, 2001; During et al., 2002; Schwarzenbach et al., 2003; Stevens et al., 2003). The term sorption is used to describe each type of attachment of a molecule on the outside surface of solids as well as on the internal surface of porous solids (Skoulikides, 1998). Depending on the type of bonding involved, sorption can be categorized as follows:

a) In physical sorption there is no exchange of electrons observed; to a small extent, intermolecular attractions between favourable energy sites and sorbing compound exist. Physisorption is caused by van der Waals forces and considered to be weak.

(b) Chemical sorption includes an exchange of electrons between surface sites and solute molecules, forming a chemical bond. In contrast to physisorption, chemisorption is considered to be strong and not always reversible.

However, the division between physical sorption and chemisorption is not always sharp. Sorption can be further subdivided into adsorption and absorption. Absorption is a physical or chemical process in which atoms, ions, or molecules enter some bulk phase, be it a gas, liquid or solid material. Adsorption is the adhesion to a surface. Adsorption can be positive or negative. Positive adsorption occurs when there is an attraction between the adsorbate and the adsorbent, resulting in a greater concentration of adsorbate at the surface-liquid interface than in the bulk solution. Negative adsorption is the opposite situation with the repelling of adsorbate (Zytner, 1992).

In the simplest case, the equilibrium distribution of a compound between a liquid phase and a solid phase can be defined as:

$$C_S = K_d\, C_W \qquad \text{[Eq. 1]}$$

where C_S (mg/kg) is the concentration of the compound in the solid phase, C_w (mg/l) the concentration of the compound in the liquid phase, and K_d the linear distribution coefficient (l/kg) which is consequently defined as:

$$K_d = \frac{C_S}{C_W} \qquad \text{[Eq. 2]}$$

Sorption in this context is related to the bulk of the sorbent and differences in sorption in heterogeneous sorbents like soils and sediments are not taken into account.

2.2.1 Sorption to natural organic matter

Sorption of hydrophobic organic compounds in natural soils and sediments occurs in general to soil organic matter (Karikhoff et al., 1979; Grathwohl, 1989). Based on this observation, the K_{OC} concept was developed that relates the sorption of a compound to the organic matter (OM), and more specific, to the organic carbon (OC) fraction in the soil or sediment. With this, the distribution coefficient K_{OM} (l/kg) can be defined:

$$K_{OM} = \frac{C_{OM}}{C_W} \qquad \text{[Eq. 3]}$$

and the more specific K_{OC} (l/kg):

$$K_{OC} = \frac{C_{OC}}{C_W} = \frac{K_{OM}}{f_{OC}} = \frac{K_{OM}}{0{,}58} \qquad \text{[Eq. 4]}$$

where C_{OM} (mg/kg) is the concentration of the compound in the organic matter, C_{OC} (mg/kg) the concentration of the compound in organic carbon, and f_{OC} (-) is the fraction of organic carbon in the soil or sediment. The factor 0, 58 accounts for the fact, that on average 58 % of the organic matter consists of organic carbon. K_{OC} values are helpful in predicting transport behavior of organic pollutants in soil. Higher K_{OC} values are associated to less mobile organic compounds while lower K_{OC} values are associated to more mobile organic substances.

K_d and K_{OC} are related to each other with the following equation:

$$K_d = K_{OC}\, f_{OC} \qquad \text{[Eq. 5]}$$

As a further simplification it was found, that a very good correlation exists between the K_{OC} and the octanol/water coefficient (K_{OW}) of a hydrophobic compound, indicating that octanol is a very good analogous to organic matter. K_{OW} values for numerous organic compounds are tabulated or can be calculated. Based on experimental results K_{OW}-K_{OC} relationships were developed as an analogous to linear free energy relationships (Karikhoff et al., 1979; Karikhoff, 1981; Chiou et al. 1979):

$$\log K_{OC} = a \log K_{OW} + b \qquad \text{[Eq. 6]}$$

and the necessary parameters *a* and *b* were determined. The K_{OW} values can then be used to calculate the respective K_{OC} values.

2.3 Sorption isotherms

For the presentation of sorption data, isotherms are used that relate the concentration of a compound in the liquid phase (C_w) to the concentration of the compound in the solid phase (C_S) at a specific temperature. Several isotherm models were introduced, that account for different sorption characteristics.

2.3.1 Linear isotherm

The simplest isotherm model is the linear model that defines the distribution coefficient K_d as presented in eq. 1. The linear sorption isotherm model is based on *Henry*'s law, which is used to calculate the solubility of gases. Sorption is assumed to be linear and concentration-independent resulting in a constant distribution coefficient K_d.

2.3.2 Freundlich isotherm

In the case of nonlinear isotherms, the empirical *Freundlich* model is often applied that accounts for a dependency of K_d on the concentration in the aqueous phase:

$$C_S = K_{Fr}\, C_W^n \qquad \text{[Eq. 7]}$$

where K_{Fr} [L/kg] and *n* [-] are the *Freundlich* sorption coefficient and the *Freundlich* exponent, respectively. The *n* value is usually less than 1 and the sorption isotherm is normally concave to the *x* axis. The coefficient *n* can be determined from the slope of a plot of log C_S versus log C_W.

The Freundlich equation does not describe sorption saturation as no plateau is reached assuming increasing water concentrations. Also the effect of temperature on sorption by the *Freundlich* model is problematic. This is because the vapour pressure or solute concentration C_W can depend on the temperature while the adsorbed mass C_S generally decreases with increasing temperature.

2.3.3 Langmuir isotherm

The Langmuir isotherm is a physically based isotherm. It describes the adsorption of a compound on a plane surface that has a limited number of equal sorption sites. Adsorption takes place in a single molecular layer and there are no interactions between neighbouring adsorbed molecules. From a kinetic point of view, the rate of

desorption from occupied sites is set identical to the rate of adsorption on the empty sites at equilibrium.

The Langmuir model is based on the assumption that the solid surface comprises a two-dimensional composition of energetic sites, and that only one molecule can adsorb on one site. The Langmuir isotherm can be defined as:

$$\frac{C_S}{C_{S,0}} = \frac{K_L C_W}{1 + K_L C_W} \qquad \text{[Eq. 8]}$$

where $C_{S,0}$ is the maximum concentration on the solid phase at full surface coverage (mg/kg) and K_L the Langmuir sorption coefficient, related to the heat of adsorption that gives an indication of the strength of bonding between the adsorbate and adsorbent.

2.3.4 BET isotherm with pore filling

The BET isotherm is, in its first part, equivalent to the Langmuir isotherm. After the first monolayer is completed, it is assumed that multilayer adsorption occurs. The molecules adsorbed in the first layer represent possible adsorption sites for additional molecules. There is no ‚saturation', the isotherm does not reach a plateau. However, the BET sorption isotherm was modified by Dubinin-Radushkevich (DR), correlated to the Eucken/Polanyi' potential model. It assumes that after multilayer adsorption capillary condensation occurs in porous sorbents and the isotherm reaches again a plateau:

$$C_S = V_0\, \rho_0\, exp\left[\frac{-RT\left(-\frac{\ln C_W}{S}\right)}{E}\right]^b \qquad \text{[Eq. 9]}$$

where V_0, ρ_0, R, and T denote the maximum volume of sorbed chemical per unit mass of sorbent [cm^3/kg], the compounds density [g/cm^3], R the ideal gas constant [J/mol/K] and T the temperature [K], respectively. C_W/S [-] is the equilibrium concentration in water normalized to the compounds solubility S [mg/L]. E [KJ/mol] is the characteristic free energy of adsorption of a compound.

2.3.5 Combined partition - pore filling model

A further model was developed to understand the role of pore filling and partition domains which occur in heterogeneous carbonaceous material (CM). The most

significant deviations from linear uptake will primarily be due to the effect of thermally changed OM, expressed by the combined Polanyi–Dubinin–Manes (PDM) sorption model. The change from partitioning to adsorption dominance depends on adsorbent concentration. Xia and Ball (1999) describe a superposition of the partitioning model and a Polanyi potential- theory-based nonlinear isotherm to fit experimental data on sorption of organic compounds in soils. The model has been adapted and incorporates now the fraction of organic carbon available for partitioning (f_{ocp}):

$$C_S = V_0\, \rho_0\, exp\left[\frac{-RT\left(-\frac{\ln C_W}{S}\right)}{E}\right]^b + f_{OCP}\, K_p\, C_W \qquad \text{[Eq. 10]}$$

with

$$K_p = \frac{1}{\gamma_{OM}\, V_{OM}\, \rho_{OM}\, S} \qquad \text{[Eq. 11]}$$

where γ_{OM}, V_{om}, ρ_{OM} and S are the activity coefficient [-] of the solute in the organic matter, the molar volume [L/mol] of the organic phase, the density of the organic matter [kg/cm³] and the aqueous solubility of the solute [mol/L], respectively.

2.4 Sorption kinetics

Due to mass transfer processes, sorption to natural sorbents is kinetically limited. This is due to the fact that many sorbents are porous and transfer of compounds out of the bulk water phase into the porosity of the sorbents is occurring by diffusion, assuming a concentration gradient. The kinetics can be defined by three steps that comprise (i) external diffusion in the bulk liquid phase, (ii) diffusion through an immobile water layer around potential sorbents, followed, (iii), by internal diffusion into a porous sorbent (intraparticlediffusion) where sorption domains may exists (intrasorbentdiffusion) (Fig. 2). In the intraparticle porosity, also surface diffusion may occur and Al-Duri and McKay (1992) stated that surface diffusion can be very significant in the adsorption process comprising up to 90% of the intraparticle diffusion (Cheng and Reinhard, 2006).

Uptake of organic compounds could therefore be fitted well using diffusion models based on Fick's second law in spherical coordinates (e.g. Ball and Roberts, 1991b).

$$\frac{\partial C}{\partial t} = D_a \frac{\partial}{r^2 \partial r}\left[r^2\left(\frac{\partial C}{\partial r}\right)\right]$$ [Eq. 12]

where C and t are the concentration (mg/l) and time (sec), respectively. D_a (cm²/sec) is the apparent diffusion coefficient, incorporating the effects of the porous medium and sorption, and r (cm) the diameter of the porous particles. Analytical solutions are available, e.g. in Crank (1975).

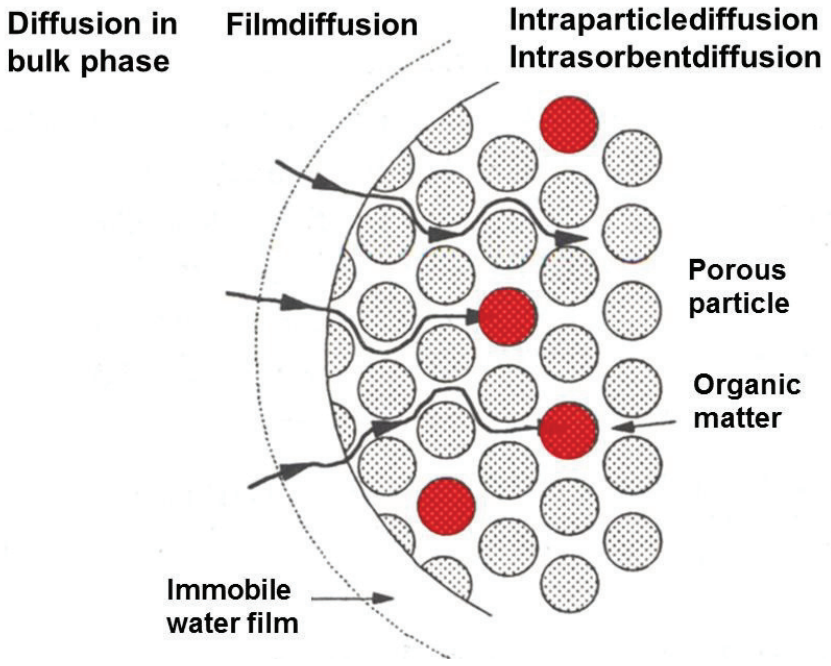


Fig. 2: Diffusion processes involved in the sorption of organic compounds in porous sorbents (modified after Schüth, 1994).

As natural porous materials may have a substantial fraction of micropores (Kleineidam et al, 2002), time scales to achieve equilibrium can be very long. Ball and Roberts (1991b) reported equilibration times of chlorinated compounds with sandy material (diameter 0,45 mm) of up to several years. The time scale was dependent on the hydrophobicity of the compounds, indicating retarded intraparticle diffusion, and on the grain size of the sorbents. The particle diameter is especially important as it is introduced in Fick's second law in spherical coordinates squared (Eq. 12).

2.5 Desorption

In principal, desorption of organic contaminants from porous sorbents is kinetically limited by the same processes as the sorption part. However, desorption of contaminants from soils and sediments are of essential importance to evaluate the

risk potential of contaminated sites. Desorption affects chemical fate, toxicity, and associated hazard to human and aquatic life. In addition it has an influence on the success of applied remediation technologies. Desorption resistance of organic contaminants and aging effect may result from the slow diffusion of contaminants in the condensed phase of organic matter (Lu, 2003). It is often observed that a small fraction of the sorbed pollutant remains in the sediment, indicating sorption irreversibility, or hysteresis. The existence of this fraction has often prevented the successful completion of remediation operations. Knowledge on sorption reversibility is therefore essential in designing remediation schemes.

The release of organic contaminants from suspended sediments to the aqueous phase has been studied widely. Rapidly, slowly and very slowly desorbing fractions have been observed (Johnson et al., 2001). A physical mechanism that may clarify slow desorption is slow diffusion, which may occur either through an organic matter matrix or through and along the walls of intra-particle pores. Many diffusion-based models hypothesize particle-scale pore diffusion processes, although direct physical evidence is lacking for typical depths of penetration for organic chemicals. Four models were investigated by Cornelissen et al., (2001) to describe the process of desorption. Two models were based on the diffusion model. The first model was based on the first order model desorption of contaminants from soil and can be summarized by the equation:

2.6 Hysteresis

Hysteresis during desorption has been either attributed to sorbent reconfiguration causing physical entrapment, or experimental artefact. Braida et al. (2003) found desorption hysteresis of benzene in charcoal and proposed a pore deformation mechanism as the reason. During sorption at high concentrations of benzene in the water phase, resulting in high benzene uptake, the charcoal is assumed to expand. At desorption, the charcoal is assumed to reconfigure at low loadings causing entrapment of some residual benzene.

Lu and Pignatello (2002) suggested pore deformation also at high concentration to be responsible for hysteresis. Sander and Pignatello (2005) introduced a method based on stable isotpes to analyse hysteresis and could demonstrate that small fractions of irreversible sorption can be detected. On the contrary, Wang et al. (2007) observed no significant hysteresis in experiments using temperature changes as the driving force for desorption.

Also pseudo-hysteresis was suggested as an explanation for an irreversible sorbed fraction (e.g. Allen-King et al., 2002; Kleineidam et al., 2004). It is assumed, that no equilibrium was established before desorption was started resulting in very slow desorption. This could also be shown by Sabbah et al. (2005) through modelling exercises. Experimental artefacts could also lead to an misinterpretation of desorption data, as system losses, either by volatilization or by sorption to e.g. vial caps, would lead to an incomplete mass balance.

In summary it has to be concluded, that the occurrence of hysteresis is still discussed controversially which is to some extend due to the lack of tailored experimental protocols.

3. SORBENTS AND CONTAMINANTS

3.1 Sorbents

The availability of sorbed hydrophobic organic contaminants and not the total amount of sorbed contaminants is critical regarding exposure, uptake or hazard of contaminants to organisms in the environment. To an enormous level, physical availability of soil-bound contaminants controls its bioavailability since the partitioning of a contaminant between the solid and water phases is a key regarding the potential for exposure and risk (Reible and Demnerova, 2001; Lu et al., 2003; Kraaij et al., 2003; Lu et al., 2004).

A fraction of sorbed contaminant is not easily desorbed, resulting in decreased availability of the desorption-resistant fraction of contaminants (Alexander, 2000; Opdyke and Loehr, 1999; Lu et al., 2003). Thus, the reversible partitioning model is no longer appropriate to explain desorption of the resistant fraction, and biphasic empirical models have been proposed to describe biphasic desorption process (Karickhoff 1980; Hawthorne et al., 2001).

The desorption-resistance has been credited to the heterogeneity of the organic matter in sediments. Besides the condensed phase carbon, related species such as hard carbon, black carbon, and glassy polymer have been extensively found in field-contaminated sediments and is assumed to be responsible for the desorption resistant fraction of contaminants in sediments (Xing et al., 1996; Huang and Weber, 1997; Gustafsson, et al., 1997; Kan et al., 1998; Xing and Pignatello, 1997; Ghosh, et al., 2001; Rockne et al., 2002).

The hard carbon content has been considered to be the main reason for desorption resistance since it displays extremely high sorption capacity as indicated by a high partition coefficients (Gustafsson and Gschwend, 1997; Ghosh et al., 2003). Organic matter is extremely condensed with the result that diffusion rates of contaminants in these phases are very slow (Ghosh et al., 2001). Usually, desorption of organic chemicals from sediment has been stated as a diffusion limited process, occurring either through the organic matter matrix or through and along the walls of narrow intra-particle pores. Thus Ghosh et al. (2001) showed that desorption resistance is related to slow diffusion from coal-derived particles. Particle scale direct observations indicate that e.g. PAHs concentrate mainly in the outer region of the coal-derived particles which suggests that it takes a long time for organic chemicals to transfer into into these particles through diffusion; this leads to the discussion that the aging effect might result from diffusion of contaminants in a definite fraction of the organic matter in sediment, where the pollutants are sequestered (Huang and Weber, 1997).

Sorbents and their chemical physical properties are a key in studying the existence of desorption resistant fraction. Therefore, different sorbents (activated carbon, charcoal, peat, zeolite Y-200) were used in the study that shows a wide variability in properties that should affect sorption-desorption behaviour.

3.1.1 Carbonaceous sorbents

Carbonaceous materials are present in many types of sediment and have a high affinity for contaminants (Chai et al., 2006; Hawthorne et al., 2007). Pure carbon is found in various structures, including graphite and diamond. Carbonaceous materials can be natural or artificial. The different types of carbons are classified into two groups: graphitic and non-graphitic depending upon the degree of crystallographic ordering and represent an intermediate between the organic origin and single crystal graphite. Non-graphitic carbons are classified also into two categories: graphitisable and non-graphitisable carbons. The types of carbon are summarized in Fig. 3.

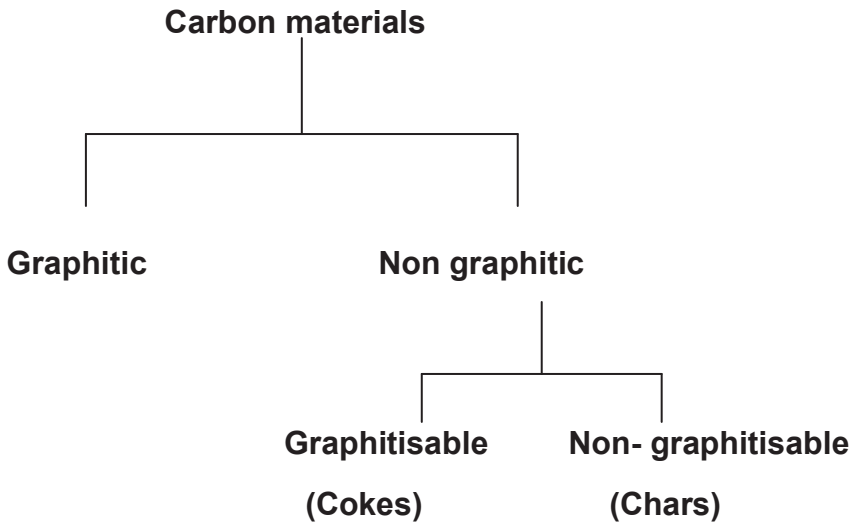


Fig. 3: Diagram illustrating the classification of carbon materials**.**

There are three basic surface heterogeneities: physical, chemical, and induced heterogeneity. Physical heterogeneities originate from geometrical differences in the size and shape such as porosity, fissures, edges, corners, and step positions on the surface. Chemical heterogeneities result from various surface functional groups including contaminants attached to the surface. Induced heterogeneity is due to the induced energy by the first bound molecule to the surface, which can affect the binding energy of the following molecules. Interaction energy between adsorbent and adsorbates normally decreases as surface coverage increases during the process of chemisorption. However, physisorption arises between adsorbed molecules on a homogeneous surface and it increases as the degree of surface coverage increases.

3.1.1.1 Activated carbon

Activated carbon (AC) is a black, solid, powdered, granular or pelletized substance. It is an excessively porous material with a large internal surface area which is known for its high capacity to bind contaminants by adsorption (Fig. 4) Specific surface areas vary between several hundred m^2 to above 1000 m^2. The first industrial production of activated carbon started in about 1900 for the use in sugar refining industries. Nearly all materials containing high fixed carbon content can potentially be activated.

It is not difficult to imagine the enormous accumulation of impurities on such a huge area in such a small volume. Pores in activated carbon have many sizes and shapes. Pore sizes have been categorized into three types: macropores (200 nm and above), mesopores (20-200 nm) and micropores (less than 20 nm).

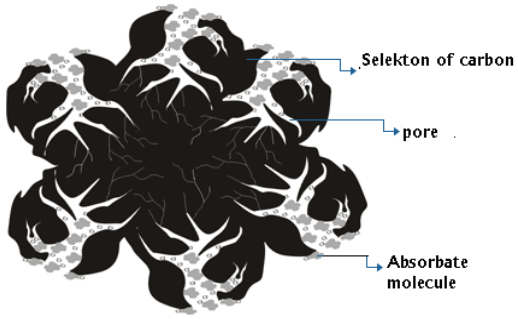


Fig. 4: Pore structure of activated carbon [(2).]

Activated carbon has a haphazard arrangement of microcrystallines with a strong cross-linking between them. They have relatively low densities and a low degree of graphitization. Activated carbons have a distinctive developed internal surface and they are usually characterized by a complex capillary structure comprising pores of different sizes and shapes. Activated carbon is widely used for commercial application as water treatment. The physicochemical properties of activated carbon depend on the starting material and the method used for its preparation. For industrial purposes, low-cost materials with high carbon and low inorganic contents are preferred as raw material for the production of activated carbon. High density of the original material and sufficient volatile content are also of substantial importance (Marín et al., 2007). The present industrial processes essentially contain the following steps: raw material preparation, low-temperature carbonization, and activation (Saad, 2007). The production conditions are sensibly planned to obtain the required pore structure and mechanical strength. The raw materials for activated carbon considered are carbonaceous materials such as peat and coals or coconut shells.

Two typical activation systems are used: gas activation and chemical activation. Starting with the primary pores existing in the raw material extra pores with favourite size distributions are formed in the activation process. Another activation method that is also used commercially is based on the use of inorganic species to reduce and dehydrate the cellulosic materials and simultaneously to stop shrinkage during carbonization. This is named chemical activation and is typically used for lignin-based feedstock such as sawdust.

A distinction is made between external and internal surface, where the internal surface is significantly higher than the external surface (Fig. 5).

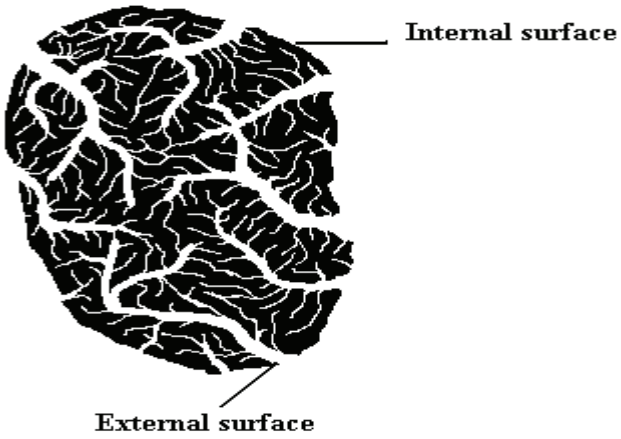


Fig. 5: External surface and internal surface of activated carbon**.**

The inorganic material contained in activated carbon is measured as ash content, normally the content ranges between 2 and 10%. Besides granulated activated carbon (GAC), powdered activated carbon (PAC) is also used commercially.

3.1.1.2 Charcoal

The first identified application of charcoal related to adsorption processes was in 3750 B.C. when Egyptians used charcoal for the reduction of ores for the manufacture of bronze. Approximately 1550 B.C., Egyptians applied charcoal for therapeutic purposes, while about 460 B.C., Hippocrates and Pliny used charcoal to treat a wide scope of infections. Around the same time, charcoal was used as filter to treat drinking water. Hence, this must have been the first use of adsorption for environmental purposes.

Charcoal is commonly made from wood that has been burnt in the absence of oxygen. Whereas charcoal is used as a material for many applications, it is found in numerous matters, from crayons to filters, its most common use is as a fuel. Charcoal

produced by the destructive distillation of wood is used as a filter, fuel, and absorbent.

3.1.1.3 Peat

Peat is an organic material that is produced in bogs. In dry form peat can be used as a fuel. In agriculture it is used to improve soil structure, increase soil acidity and preserve moisture during dry periods. Peat can be also used as water filtration material and in chemistry; peat is used as a natural ion exchanger.

In comparison to AC and charcoal, sorption on peat is relatively low and the bioavailability of contaminants like polycyclic aromatic hydrocarbons (PAHs) in soil is increased by the presence of peat components (Bogan and Sullivan, 2003; Haderlein et al., 2001).

3.1.2 Zeolites

Zeolites are microporous, aluminosilicate minerals mainly used in ion exchange processes, molecular sieving and catalysis. Zeolites form a structure of uniform pores and / or channels, which allow only small molecules to pass; therefore they serve as molecular sieves. Zeolites are natural minerals with a rigid structure (Fig. 6), but can also be produced synthetically for specific uses.

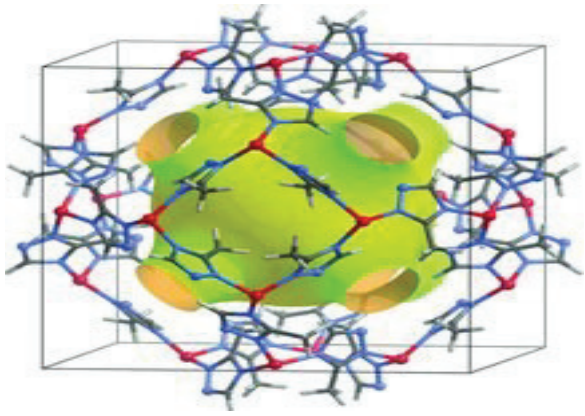


Fig. 6: Rigid structures of Zeolite [(3).]

The adsorption of aromatic molecules in zeolitic microporous materials is of great scientific interest because of applications in separation technology and catalysis. For example the separation of p-xylene from C aromatic mixtures are achieved on an industrial scale by using selective adsorption in synthetic faujasite type zeolites (Lachet 1997).

The classification of pores in zeolites is simplified by using the term primary porosity which is referring to the cavities and channels forming the zeolite matrix, and secondary porosity to characterize the macroporosity and mesoporosity developed

between the zeolite crystals. Adsorption in the primary porosity of zeolites is regarded as volume filling of the zeolite microporous adsorption space, which occurs rather than a layer-by-layer surface coverage (Roque-Malherbe 2000). The shape-selective properties of zeolites are also the base for their use in molecular adsorption. The capability to specifically adsorb certain molecules has opened up a wide scope of molecular sieving applications. Occasionally it simply depends on the size and shape of pores, if molecules can enter into the zeolite. In other cases different forms of molecules enter the zeolite but some diffuse through the channels more rapidly, leaving others stuck behind, as in the purification of xylene by silicalite Figure 6 shows exemplary the sorption of chlorinated hydrocarbons in zeolite.

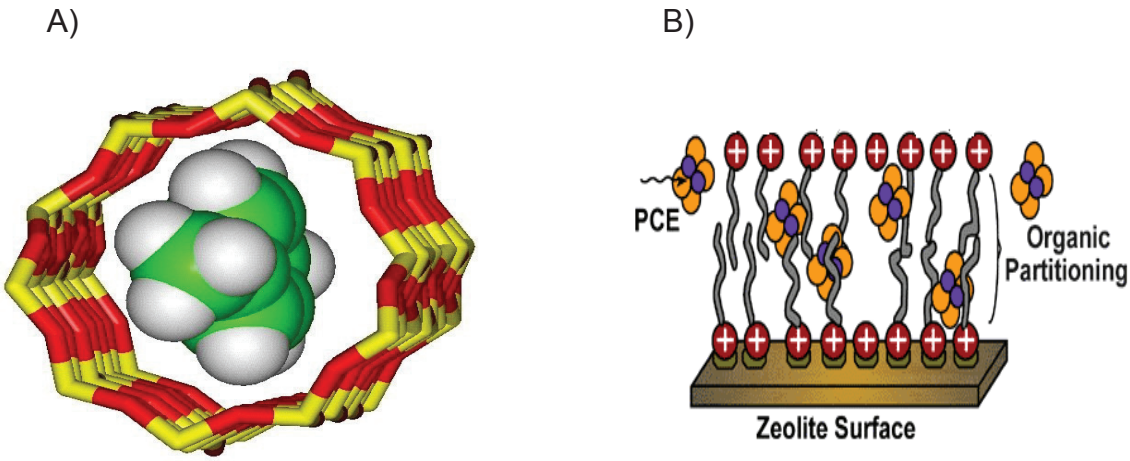


Fig. 7: a) Due to its shape xylene can diffuse freely in the channels of silicalite b) The shape of PCE sorbed in zeolite[3].

The zeolite micropore volume coverage describes the fraction of the volume filled with adsorbed molecules. The adsorption isotherm equations used to describe adsorption in the zeolite primary porosity, are the basis for describing the filling of the zeolite microporous adsorption space. The adsorption process in zeolites is regarded as a physisorption process, because the interaction between sorptive and sorbent can be considered as a Van der Waals type interaction. Zeolites make up complex adsorption systems. Both terms adsorption and sorption are used to describe the pore-filling process for zeolites. Adsorption in zeolites can take place 1) in micro pore filling, 2) At high pressures, surface coverage consisting of monolayer, multilayer adsorption and capillary condensation occur on the walls of meso- and macropores (Roque-Malherbe 2000).

Immobile adsorption takes place when the adsorbed molecule is forced to vibrate around an adsorption site (Roque-Malherbe 2000). The special adsorption properties of zeolites are due to their unique surface chemistries. The primary structural units of

zeolites are the tetrahedra of SiO_4 and AlO_4. Here, the aluminum and silicon atoms are linked together by oxygen atoms. Zeolites tend to be hydrophobic and thus sorb non-polar molecules. In general, as the aluminium content decreases the zeolites' affinity for water decreases (Pope, 1987). Zeolites with high SiO_2/Al_2O_3 ratios have been shown to remove organics from water (Anderson, 2000; Giaya et al., 2000).

Types A, X, and Y –zeolites are the main zeolites and molecular sieves that are in commercial use for adsorption and ion exchange. In type A the ratio of Si/Al is normally one while those in types X and Y is typical one to five. The aluminium atom can be removed and replaced by silicon in some zeolites, thereby reducing the number of cations. The cations can also be exchanged.

Selectivity for molecules is also depending on pore size and shape. Molecules that are larger than the pore diameter of the zeolite are excluded from the internal spaces (Anderson, 2000; Giaya et al., 2000). Molecules that are able to enter the zeolite can interact with the zeolite through van der Waals, electrostatic and other interactions.

3.2 Contaminants

The presence of the synthetic chemicals in the environment is receiving more attention from researchers. This is due to health risks posed by the synthetic chemicals and the pool of information available in literature on the behaviour of these chemicals in the environment (Zytner 1992). Anthropogenic generated pollutants are widely distributed and of large concern (Fig. 8)

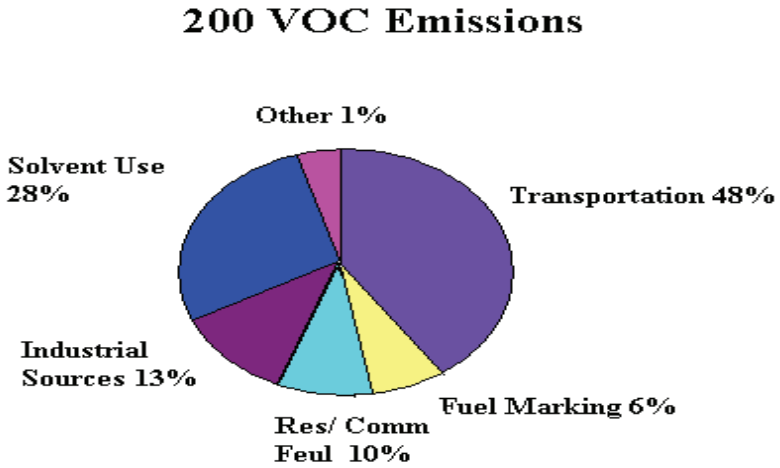


Fig.8: Major anthropogenic sources of concern of VOC in Canada (CCME).

3.2.1 Trichloroethylene

Trichloroethylene (TCE) is a halogenated, aliphatic organic compound. Its properties are listed in Table 3. TCE is a colourless liquid with a slightly sweet smell. TCE is

used in metal degreasing, textile cleaning, solvent extraction processes and as a carrier solvent (WHO, 1985; Hawley, 2003).

In recent years, industries have grown extremely, exposing groundwater and aquifers to intense risks of being polluted with TCE. This compound is unpredictably released into the environment. It undergoes many processes inclusive adsorption onto soils, volatilization, desorption and transformation (Bedient et al., 1994).

Partitioning of TCE from surface waters to air is quick with a half-life of numerous days to several weeks (CEPA, 1993). Evaporation is the main process of elimination of TCE from surface waters while photo oxidation, hydrolysis and biodegradation play a minor role (CEPA, 1993). The conditions might be different in groundwater, where TCE may be biotransformed under appropriate anaerobic conditions into dichloroethylene, chloroethane and vinyl chloride with a biodegradation half-life ranging from several months to several years. Volatilization to the atmosphere is also the main process of elimination of TCE from the soil. The process is comparatively fast but slower than from surface waters. Under anaerobic conditions TCE may biotransfer to vinyl chloride which is far more toxic than TCE. In many areas vinyl chloride has been found on site, signifying that this transformation is happening. Danger management activities need to address not only the danger posed by TCE itself but also TCE as a precursor of vinyl chloride. (Hugh et al, 1992)

Trichloroethylene is very mobile in soil. The movement is principally affected by the organic carbon content (OC) which effects sorption to the soil. Experimentally calculated sorption coefficients (K_{oc}) for TCE in soils are ranging from 106 to 460 (Garbarini and Lion, 1986, cited in ATSDR, 1995). TCE density is greater than water and it tends to settle at the aquifer base. From these pools, TCE may be slowly released over long periods of time.

The indications of exposure to TCE are manifested as central nervous system problems (WHO, 1985). They include headache, drowsiness, hyperhidrosis and tachycardia. In more severe cases coma may result. Psychomotor impairment was observed after inhalation when exposed to 5,400 mg/m^3 for two hours in work place conditions (WHO, 1985). TCE vapours can be the also reason for eye irritation. High oral doses can be toxic to the liver and kidneys (WHO, 1985).

The Environmental Protection Agency (EPA) defined as a maximum contaminant level 5 µg/L of trichloroethylene (TCE) for drinking water. TCE is quickly absorbed as soon as it is inhaled; 37-64% of the inhaled TCE is taken up in the lungs. Once TCE is in the body it is distributed and accumulates in tissue. TCE exits the body unchanged in exhaling air and to a lesser degree in feces. TCE, however, may be rapidly metabolized in the liver (ASDR1995).

3.3.2 Tetrachloroethylene

Tetrachloroethylene (PCE, perchloroethylene) is one of the five most often identified volatile organic compounds found in municipal groundwater supplies (Ryoo et al., 2000). Tetrachloroethylene is a manufactured chemical that is extensively used in the dry-cleaning of textiles. Other names for Tetrachloroethylene include PERC, perchloroethylene, Tetrachloroethylene and PCE. Its properties are listed in Table 4.

Microbial degradation of PCE does primarily occur anaerobically by reductive dehalogenation to less chlorinated ethylenes trichloroethylene (TCE), dichloroethylene (DCE), vinyl chloride (VC) and ethylene as well as to ethane. The dechlorination of PCE is incomplete when it does occur with VC and cis-DCE formed primarily. However, dehalorespiration of PCE to ethylene is probable. Vinyl chloride is a known human carcinogen and both VC and cis-DCE are US EPA priority pollutants.

Similarly to TCE PCE transport depends on physical processes like volatilization and sinking due the effect of gravity, as well as chemical and biological degradation processes (Mouvet et al., 1993).

3.3.2 Xylene

Xylene is an aromatic hydrocarbon with two methyl groups attached. The properties of xylene are listed in table 3. Three isomers exist: *p*-xylene, *o*-xylene, and *m*-xylene. The extreme complexity in separating these isomers has led to one of the most interesting subjects in the oil industry because extraction is only possible for removing *o*-xylene but fails in the other two isomers because of the similarity of their boiling points. Temporarily, these isomers are very poisonous volatile organic compounds (VOCs) and failure in separating them from the industrial discharges results in the release of the mixture during attempts to separate xylene isomers (Wu and Yang, 2009).

One of the earliest effects of exposure to xylene are increased liver enzymes. Other effects of a single or short time exposure include irritation of nose, eyes, and throat, headache, nausea, dizziness, vomiting, fatigue, light-headedness, irritability, loss of appetite, reduced coordination, abdominal pain and loss of consciousness (ATSDR 2007).

4. MATERIALS AND METHODS

4.1 Materials

Four different sorbents were used in the experiments, three carbonaceous materials, an activated carbon (F-100, Chemviron), a commercial charcoal (Chemviron 'Sommerhit'), a peat, and a synthetic Y-type zeolite with silicon to aluminum ratio of 200 and a pore diameter of 0.74 nm (Degussa AG). Zeolites with high Si/Al ratios are hydrophobic and have a strong affinity for nonpolar molecules, e.g., organic compounds. Zeolites with low Si/Al ratios are hydrophilic and have a strong affinity for polar molecules. The transition from a more hydrophilic to a more hydrophobic structure occurs at a Si/ Al ratio of 7-10 (Flanigen, 1985). All carbonaceous sorbents were oven dried at 60°C for eight hours and pulverized with a planet ball mill to minimize equilibration time. The synthetic zeolite Y-200 was used in its powdered form as received. Grain size analysis revealed grain sizes less than 0.063 mm.

Sorption and desorption experiments were conducted with two pairs of organic contaminants, an aliphatic couple (TCE/PCE) and an aromatic couple (o-Xylene/p-Xylene). Compounds were obtained as pure products from Aldrich Corp. and used as received. Concentrated methanol stock solutions were prepared and spiked to the samples as needed. Methanol concentrations in the aqueous solutions of the samples were always less than 0.5%, a level at which methanol has no measurable effect on sorption (Nkedi-Kizza et al., 1987). A summary of the chemical and physical properties is given in Table 4.

Table 4: Physical properties of contaminants.

Sorptive	**TCE**	**PCE**	**o-xylene**	**p-xylene**
Density, g/mL	1.46	1.6227	0.8610	0.8802
Solubility at 20°C, mg/L	1000	150	175	198
Henry's Law Constant, atm-m^3/mol 20°C	0.0089	0.018	0.005	0.007
Molecular Weight, g	131.4	165.83	106.16	106.16
Boiling Point °C	86.7	121	144.41	138.37
Melting Point °C	-73	-19	-25	-25
Vapor Pressure 20°C, mm	57.8	18.47	27.3	27.3

Hg				
Log K_{ow}	2.42	3.4	3.12	3.17

4.2 Analytical methods

4.2.1 Characterization of the sorbents

The sorbents were characterized according to the procedure described in Kleineidam et al. (2002). In brief, the organic carbon content oc [%], as well as the nitrogen and hydrogen contents of the samples were determined by elemental analysis (Vario EL, Elementar). The fraction of black carbon was determined according to the direct high-temperature oxidation method from Gustafsson and Gschwend (1998). The samples were heated for 24 h at 375 °C, and the remaining fraction was analyzed again for C, H, and N. The difference between black carbon and oc was assumed to be available for partitioning (f_{ocp}). The specific surface area SA [m²/g] and the meso- and microporosity IP [cm³/kg] were determined using nitrogen adsorption and the BET method (Micromeritics ASAP 2010).

Particle density was measured using an AccuPyc 1330 Pycnometer (Micrometrics). In this method the principle of gas (helium) displacement is used to determine the particle density. Bulk density was measured using a GeoPyc 1360 (Micrometrics).

A summary of the chemical and physical properties of the sorbents is given in Table 5.

Table 5: Properties of the sorbents

	OC Content (%)	**N_2 Content (%)**	**OC Content (%)[1]**	**N_2 Content (%)[1]**
Activated carbon	88,9	2,38	71,21	0,43
Charcoal	81,23	1,06	22,4	0,21
Peat	33,1	2.7	2,1	0,54

[1] After heat treatment at 375 °c for 24h.

4.2.3 Chemical analyses – Gas chromatography

A gas chromatograph (Agilent 6890) equipped with an electron capture detector (ECD) and a flame ionisation detector was used for the analyses of the organic contaminants. In a GC, a capillary column with a stationary phase that is placed in an oven is used to separate a mixture of compounds based on their different affinities for the stationary phase. The compounds are introduced into the GC either in a liquid or as a gaseous sample with syringes and flushed through the column with a carrier

gas. Each compound has a specific retention time in the column that can be used to identify the compound based on standard runs. Besides the column stationary phase, other parameters can be used to alter the retention time such as oven temperature and carrier gas flow rate.

Compounds are detected at the end of the column with an appropriate detector. In the case of TCE and PCE, the ECD as well as the FID can be used for detection, with the ECD having the much lower detection limit. For the Xylenes, only the FID was used for detection.

Samples were introduced into the GC in the gasphase using gas-tight syringes. This is possible, as the organic compounds have relatively high Henry's law constants (Table 4). The injected volume was in general 200 µl. Compared to solvent extraction of the organic compounds out of the water, this type of analyses has several advantages. There is no sample preparation necessary, in general no interference with other compounds or the solvent is given, and a repeated injection of the gas phase is possible.

For calibration of the GC and spiking of the samples, two concentrated methanol stock solutions were prepared for each compound with a concentration of 10 g/l and 100 g/l, respectively. GC Standards were prepared by injecting 4 µl to 8 µl of the 10 g/l stock solution and 15 µl to 25 µl of the 100 g/l stock solution in 20 ml glass vials containing 18 ml of distilled water and capped with Teflon lined butyl rubber septa. For the establishment of the calibration curves, 200 µl gas samples were injected into the GC, analogous to the sample vials

4.3 Experimental procedure

Experiments were conducted in triplicate in 22 ml crimp top glass reaction vials and performed in four steps, (i) sorption of one compound, (ii) desorption of that compound, (iii) sorption of the complementary compound, and, (iv), final extraction of the sorbent. In addition, (v), binary sorption isotherms were established by adding the complementary compounds simultaneously.

(i) For the first sorption step, 20 ml of deionized water and varying amounts of the pulverized sorbents (typically less than 100 mg) were added to the glass vials leaving a headspace of about 2 ml. Target compounds were injected and vials were capped with PTFE lined butyl rubber septa. Reference vials containing no solids were prepared identically. Vials were kept at room temperature (20°C ± 2°C) in the dark and shaken frequently. A time period of 7 days was found to be sufficient to establish sorption equilibrium with such pulverized materials (Kleineidam et al. 1999), and samples were analyzed thereafter. Concentrations of contaminants in the aqueous phase were determined by analyzing the gas phase in the headspace of the vials. In general, 200 µl of gas phase were injected into an Agilent GC (model 6890) equipped with an ECD and FID. Aqueous concentrations were then calculated based on

external standards prepared identical to the samples. Sorbed concentrations were calculated based on the aqueous concentrations measured in the reference vials to establish sorption isotherms.

(ii) For the following desorption step the vials were opened and placed on a sand bath kept at 40°C. In addition, nitrogen was bubbled through the water in the vials to accelerate desorption. After two weeks, vials were capped again and headspace concentrations of the desorbed compounds were measured one to three days later. In case of concentrations above the detection limit, vials were opened again and desorbed as described for another 2 weeks. This was continued until headspace concentrations were below the detection limit.

(iii) Prior to the second sorption step, the evaporated water was replaced by adding an appropriate amount of deionized water. Then, the complementary compound was spiked to the samples and vials were capped. After 7 days, concentrations of the initial compound and the complementary compound in the aqueous phase were determined by analyzing the gas phase in the headspace of the vials.

(iv) Finally the water phase in the vials was replaced by 5 ml of methanol and vials were kept at 40°C on the sand bath for final extraction. After 4 weeks, methanol concentrations of the compounds were measured and the final desorbed mass calculated.

5. RESULTS

In the following, the results of the laboratory experiments on the sorption and desorption of the selected organic contaminants on the sorbents are presented. First, the equilibrium sorption isotherms with the single compounds and the binary sorption isotherms are presented. Then, the results of desorption and respiking experiments are discussed. Finally, the concluding methanol extractions of the sorbents after the sorption desorption and respiking steps are presented.

Based on these data, the fractions of irreversible sorption for each combination of sorbent and contaminant are calculated based on mass balance considerations and compared.

5.1 Single isotherms

In the sorption experiments of all sorbents (activated carbon, charcoal, peat, zeolite Y-200) with all contaminants (TCE, PCE, o-Xylene, p-Xylene) a nonlinear relation between the concentration in the water phase C_W and in the solid phase C_S was observed. Therefore, the nonlinear *Freundlich* isotherm model (eq.7) and the Polanyi Manes model (eq. 10) combing a partition part and a pore filling part were fitted to the sorption data and the isotherm parameters calculated.

Fig. 9 to Fig. 12 shows the sorption data and the *Freundlich* isotherms fitted to the data. In Table 6 the *Freundlich* data for all isotherms are summarized

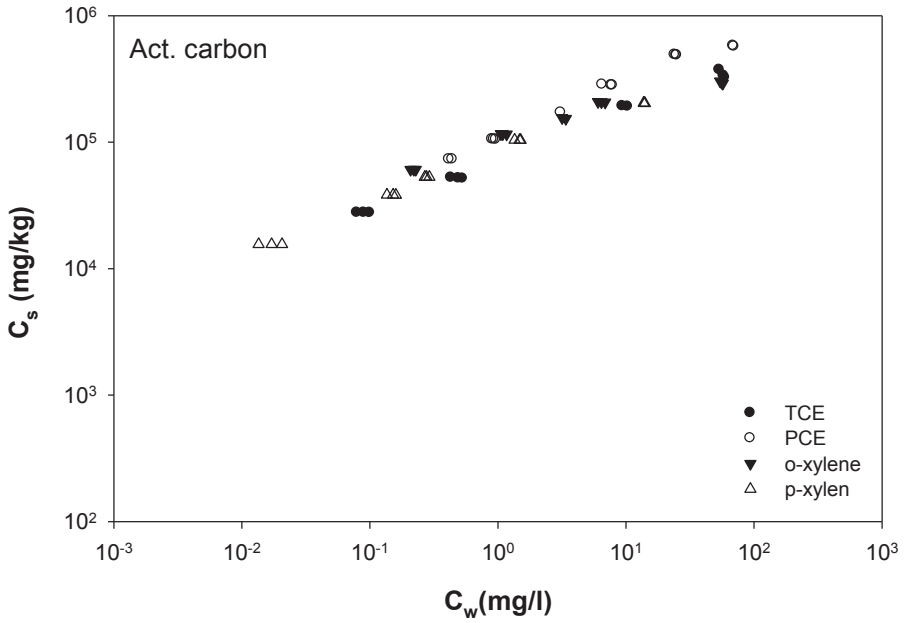


Fig.9: Sorption data for PCE, TCE, o-Xylene and p-Xylene for activated carbon and fitted *Freundlich* isotherms.

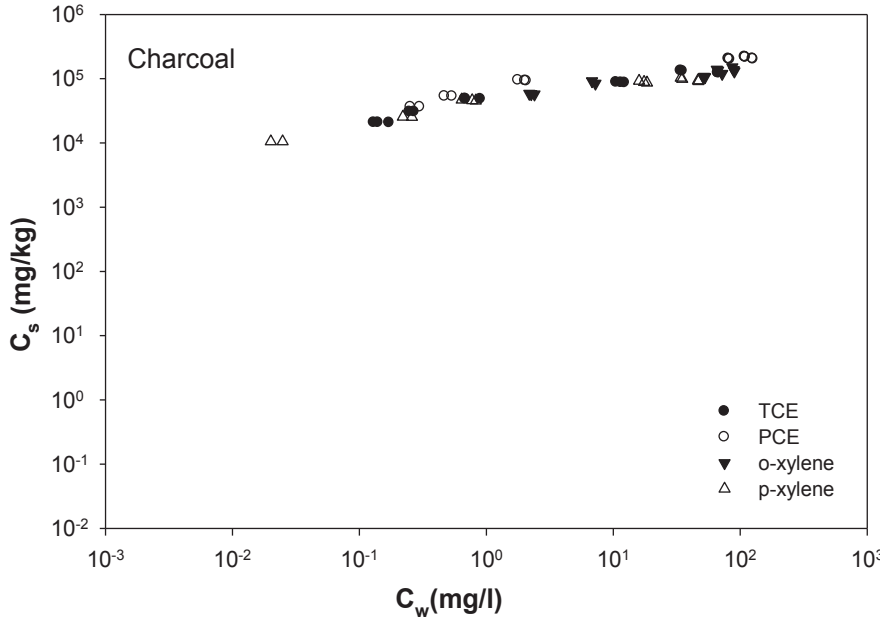


Fig.10: Sorption data for PCE, TCE, o-Xylene and p-Xylene for charcoal and fitted *Freundlich* isotherms.

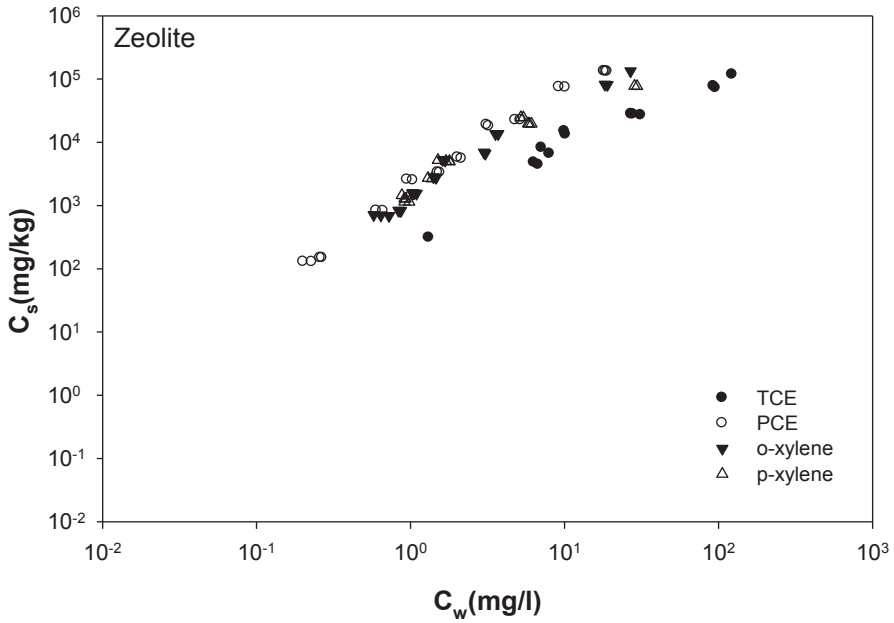


Fig. 11: Sorption data for PCE, TCE, o-Xylene and p-Xylene for Zeolite y-200 and fitted *Freundlich* isotherms.

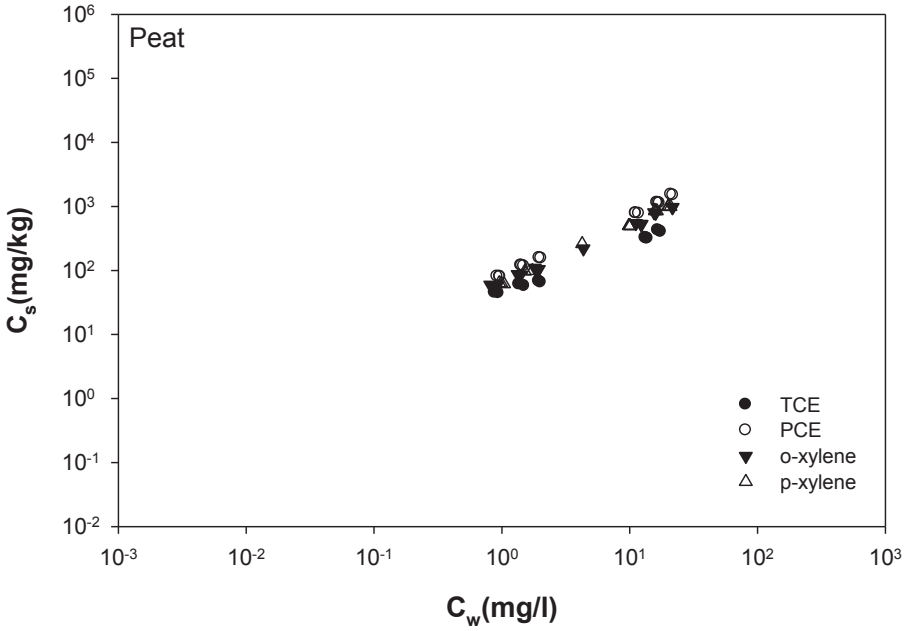


Fig. 12: Sorption data for PCE, TCE, o-Xylene and p-Xylene for peat and fitted *Freundlich* isotherm.

Table 6: Freundlich sorption parameters of single compound isotherms**.**

		Act. Carbon	Charcoal	Zeolite	Peat
TCE	**K_f [L/kg]**	70820	42690	560	46
	1/n [-]	0.39	0.28	1.14	0.76
	r^2	0.99	0.95	0.93	0.99
PCE	**K_f [L/kg]**	110550	63030	1740	83
	1/n [-]	0.43	0.26	1.66	0.92
	r^2	0.98	0.96	0.98	0.99
o-xylene	**K_f [L/kg]**	105430	50620	1460	640
	1/n [-]	0.28	0.21	1.43	0.88
	r^2	0.96	0.92	0.97	0.99
p-xylene	**K_f [L/kg]**	80690	38390	1880	63
	1/n [-]	0.38	0.28	1.24	0.91
	r^2	0.99	0.95	0. 94	0.99

In general, the highest sorption was found for the activated carbon, followed by charcoal, zeolite and peat. The order in sorption capacity for the organic sorbents increases in their order of carbonization, as expected (Xing et al. 1994; Xing et al., 1999; Chefetz et al., 2000). Other authors (Johnson et al., 2001; Simpson et al., 2003) found that a high degree of nonlinearity can be related to the level of aromaticity of the sorbent. Sorption capacity of PCE, p-xylene and o-xylene onto peat are almost the same, which is due to the very similar polarities of the species (Kile et al., 1995). The Freundlich exponent (n) as a measure for the nonlinearity of the isotherms was for the charcoal as well as for the activated carbon in all cases significantly below 0.5. The isotherms for the zeolite Y-200 show a sharp increase at low concentrations in the aqueous phase and thus the Freundlich exponent is significantly greater than 1. The Freundlich sorption coefficient and exponent for TCE on activated carbon and charcoal are comparable to those reported by Kleineidam et al. (2002) who worked on the same sorbent materials and TCE.

Fig. 17 to Fig. 20 shows the first sorption data and the Polanyi Manes isotherms fitted to the data.

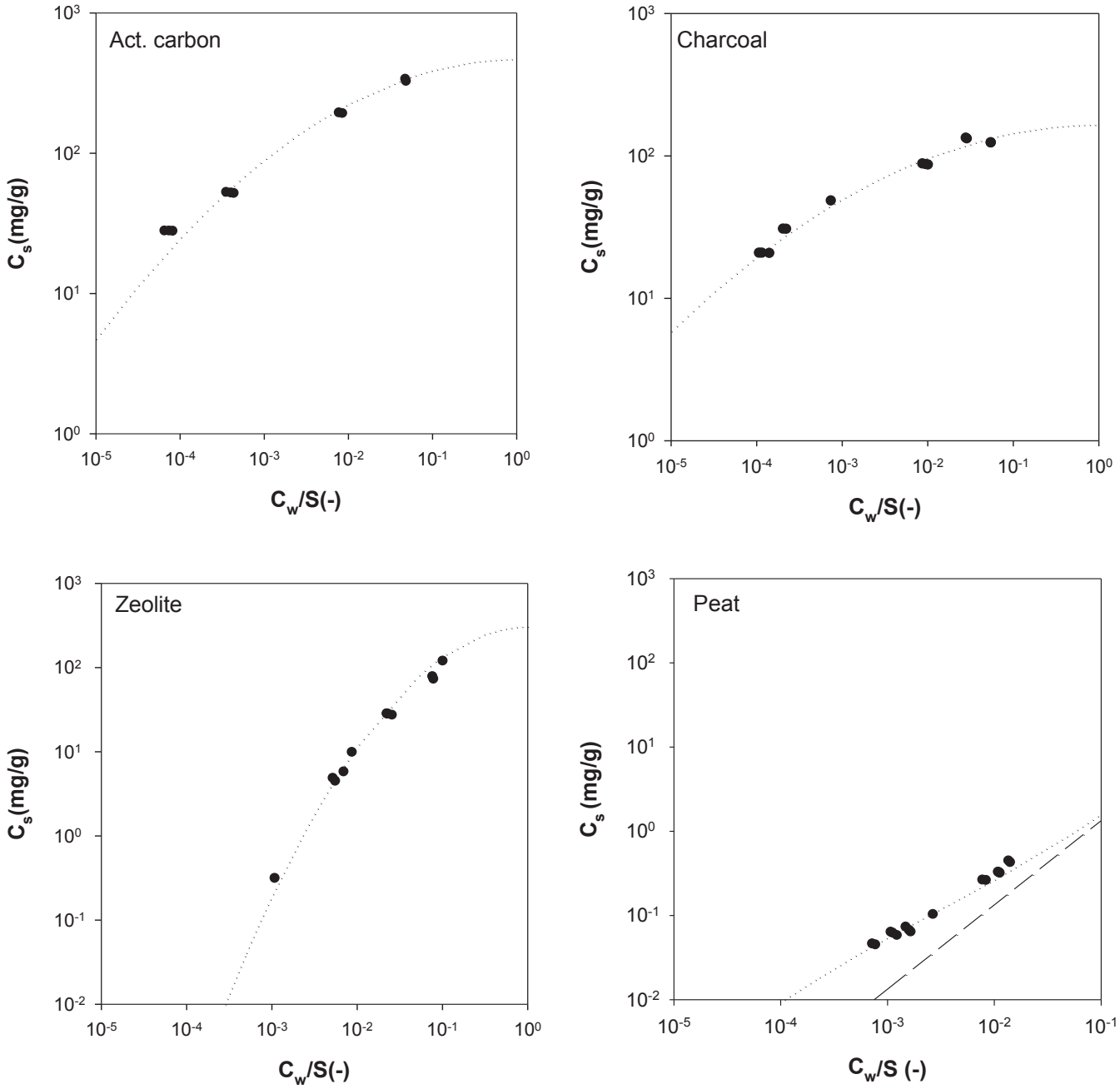


Fig.13: Sorption data for TCE on activated carbon, charcoal, peat and zeolite Y-200 and the fitted Polanyi Manes isotherms. Dotted line indicates pore filling part, dashed line indicates partition part.

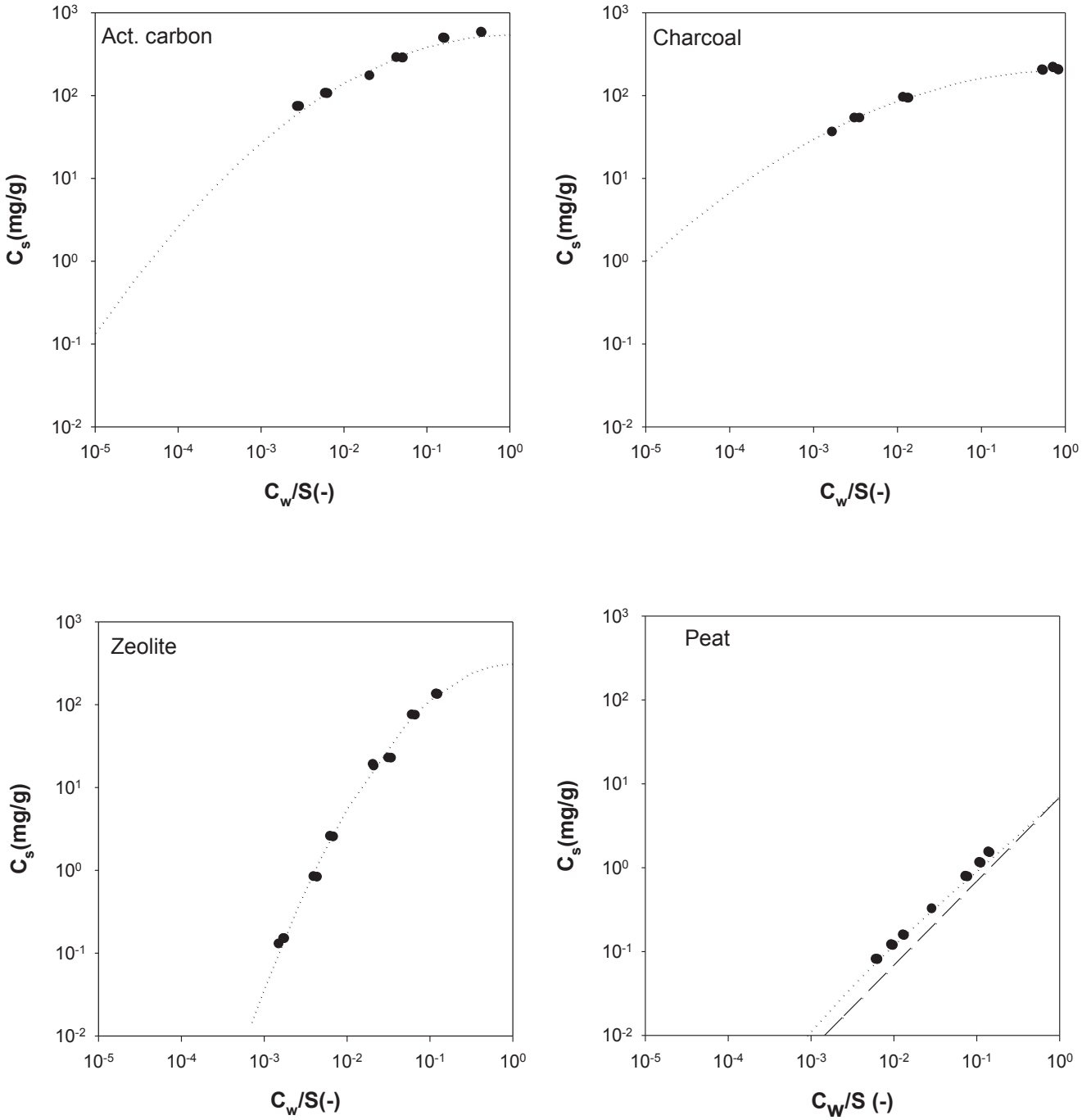


Fig.14: Sorption data for PCE on activated carbon, charcoal, peat and zeolite Y-200 and the fitted Polanyi Manes isotherms. Dotted line indicates pore filling part, dashed line indicates partition part.

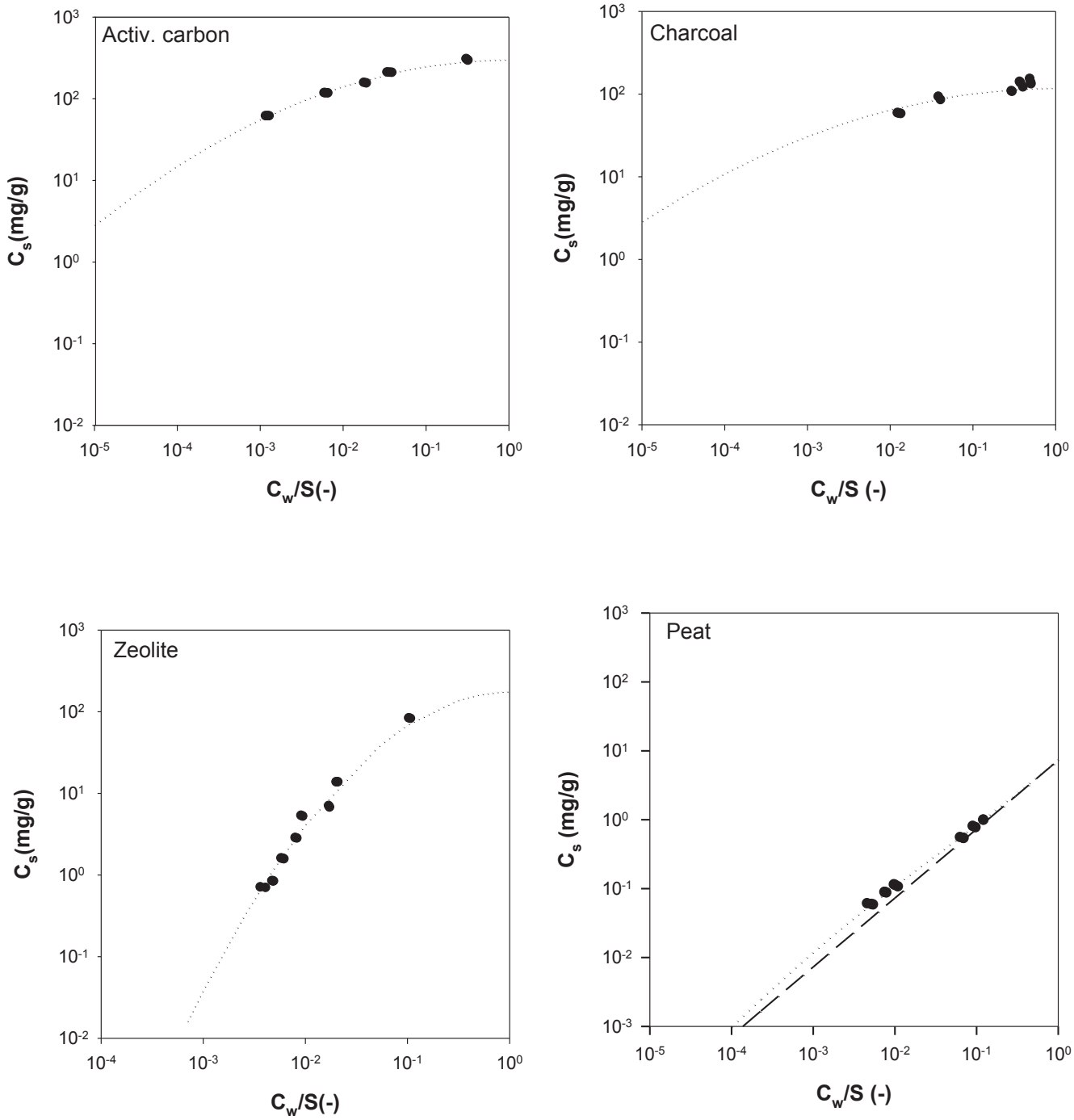


Fig.15: Sorption data for o-Xylene on activated carbon, charcoal, peat and zeolite Y-200 and the fitted Polanyi Manes isotherms. Dotted line indicates pore filling part, dashed line indicates partition part.

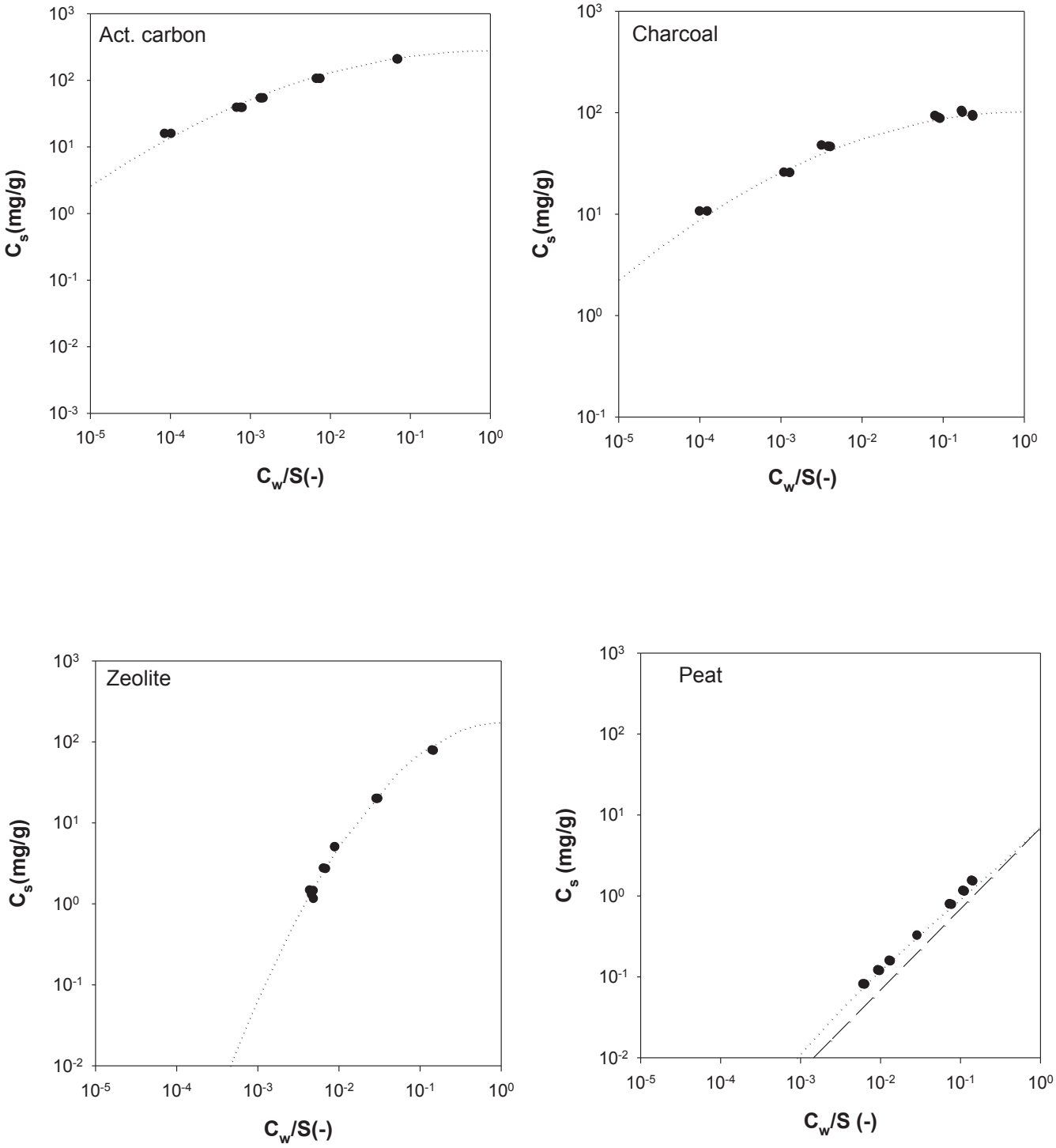


Fig.16: Sorption data for p-Xylene on activated carbon, charcoal, peat and zeolite Y-200 and the fitted Polanyi Manes isotherms. Dotted line indicates pore filling part, dashed line indicates partition part.

Parameters determined for the Polanyi-Manes dual-mode isotherm model are listed in Table 7.

Table 7: Polanyi-Manes model parameters for sorption of a single compound.

		Act. Carbon	Charcoal	Zeolite	Peat
TCE	**V_0 [cm³ kg^{-1}]**	322	123	205	0.22
	E_0 [kJ mol^{-1}]	13.6	15.6	6.6	11.5
	K_p[Lkg^{-1}]	0	0	0	9.13
	r^2	0.31	0.17	0.9	0.08
PCE	**V_0 [cm³ kg^{-1}]**	334	125	192	0.23
	E_0 [kJ mol^{-1}]	9.9	12.4	5.7	8.1
	K_p[Lkg^{-1}]	0	0	0	48.53
	r^2	0.15	0.07	0.94	0.14
o-xylene	**V_0 [cm³ kg^{-1}]**	335	135	205	0.22
	E_0 [kJ mol^{-1}]	13.1	13.4	6	8.9
	K_p[Lkg^{-1}]	0	0	0	32.33
	r^2	0.03	0.102	0.96	0.11
p-xylene	**V_0 [cm³ kg^{-1}]**	332	121	204	0.23
	E_0 [kJ mol^{-1}]	13.5	14.9	6.1	9.9
	K_p[Lkg^{-1}]	0	0	0	33.77
	r^2	0.59	0.08	0.6	0.54

In the Polanyi-Manes model, the adsorption part is obtained after subtraction of the partitioning part. E and V_0 are fitting parameters. The model fits to the parameters K_p, V_0 and E along with the calculated mean weighted square errors for all chemicals with activated carbon, charcoal, peat and zeolite. The fitted lines are in a good agreement with the overall observed sorption data and adsorption components. This means that the total sorption data and the adsorption component can be modeled by the Polanyi-Manes model. For most isotherms the hole-filling mechanism actually predominates over the partitioning part. Also, V_0 values are similar for all compounds for one sorbent, indicating that the total porosities are filled by the compounds.

Values of E are in the range of 5.7- 15.6 KJ mol $^{-1}$ in accordance to values reported by Kleineidam et al. (2002).

The nature of the adsorption sites in glassy polymers has been described as voids (Vieth, 1991, Vieth, 1992) inside the polymer matrix. Partitioning combined with an array of pore-filling adsorption sites having different energies can lead to an isotherm that corresponds in shape with the Freundlich isotherm (Weber et al., 1992). It is shown that the surface area of activated carbon is higher than that of charcoal which in turn is higher than that of the peat. This is reflected by the different sorption capacities. Expectedly, the peat isotherm shows a more linear isotherm which can be attributed to the predominance of the partition part of the sorption. At low concentration isotherms are nonlinear, and with increasing concentrations become linear which means that at low concentration sorption is dominated by partitioning and at high concentrations by pore-filling. The isotherm nonlinearity observed for peat at low concentrations cannot easily be attributed to adsorption to a mineral surface (Spulock and Biggar, 1994; Pignatello, 1991; Weber et al. 1992; Beck et al., 1993; Murphy et al., 1994; Young 1995). It was shown that, possibly, specific sorption occurs at internal sites (Pignatello, 1991) analogous to sorption that takes place in glassy organic polymers (Berens, 1989; Cain et al., 1993; Tascano et al. 1993; Horas and Nieto, 1994).

In the following the results of the binary sorption experiments (Table 8, 9 and Fig. 17-20) are shown and discussed.

Table 8: Results of the binary sorption experiments. (i) sorption of a single compound on a sorbent (ii) sorption of the compound in a binary sorption system with a corresponding contaminant (Freundlich Parameter).

sorbent	sorptive	Kf [L/kg]	1/n [-]	sorptive in a binary system	Kf [L/kg]	1/n [-]
Activated carbon	**TCE**	70820	0.39	**TCE**	31760	0.37
	PCE	11055	0.43	**PCE**	70370	0.47
	o-xylene	10543	0.28	**o-xylene**	28070	0.56
	p-xylene	80690	0.38	**p-xylene**	42500	0.48
charcoal	**TCE**	42690	0.28	**TCE**	14000	0.49
	PCE	63030	0.26	**PCE**	14490	0.41
	o-xylene	50620	0.21	**o-xylene**	25290	0.27
	p-xylene	38390	0.28	**p-xylene**	21830	0.48
peat	**TCE**	46	0.76	**TCE**	22	0.92
	PCE	83	0.92	**PCE**	69	0.89
	o-xylene	64	0.88	**o-xylene**	61	0.855
	p-xylene	63	0.91	**p-xylene**	58	0.83
zeolite	**TCE**	560	1.14	**TCE**	143	1.43
	PCE	174	1.66	**PCE**	290	2.42
	o-xylene	1460	1.43	**o-xylene**	147	1.41
	p-xylene	1880	1.24	**p-xylene**	270	1.61

Freundlich coefficients decreased in the binary solution between 5 % - 17 % for peat and between 45 %- 52 % for charcoal. The decreasing trend in Freundlich coefficient K_f for the organic sorbents is as follows: charcoal > activated carbon > peat. High reduction in *Freundlich* coefficients of the sorbents in binary solution systems suggests that there was adsorption competition among adsorbents not only onto adsorbent surfaces.

Competitive effects may be dependent upon both the similarity of physicochemical properties of the sorbent and the characteristics of the sorbents (Huang et al., 2003; Pignatello et al., 2006; Zhang et al., 2010). Sorptives have to compete to be

adsorbed in a binary system. However, some researchers reported no competitive sorption for a binary system (Chiou and Kile, 1998).

Studies found that a solute sorbed on organic material can be displaced partially by a second solute and that the sorption capacity, isotherm nonlinearity, and desorption rate of a given HOC solute are all affected differently by additional HOC solutes (White and Pignatello, 1999; Xia and Ball, 2000; Sander and Pignatello, 2005).

For OM having different energy sites, the net driving force for an obviously dominant bi solute in a binary system may well result in preventative occupation of a large fraction of the highest energy sites. This can happen even though single molecules of the target solute are more sorbable than those of the bi-solute if there are sufficiently more of the co-solutes present to produce a larger total entropic energy force driving the target solute from solution phase. In that case, larger percentages of the sorbed solute would be forced to occupy lower energy sites in the bi-solute system than they would do in a comparable single solute system. This would be increasingly the case with increasing sorbability of the bi-solute. There are proportionately lower densities of high energy sites for a target solute in single-solute systems of very high concentration and, thus, proportionately larger percentages of that sorbate must sorb at lower energy sites. High energy sites are usually more abundant in glassy polymeric matrixes than they are in rubbery matrixes (Weber et al. 2002). Charcoal, activated carbon and zeolite may therefore have higher numbers of high-energy sites per unit mass than peat, a greater percentage of them are likely to be more readily accessible to sorbates. OM matrixes of the young materials are more highly amorphous and present less resistance to diffusive transport of sorbate molecules to such reactive sites.

Freundlich *n* values for sorption of all contaminants were increased in the presence of the second contaminant for all four sorbents. This may be due to the swelling of OM matrixes in the presence of the second contaminant, OMs are transformed temporarily to more rubbery states, thus causing enhanced partitioning type linear sorption. This explanation is in agreement with the observation by Xia and Ball (2000) that partitioning becomes a more significant contributor to the sorption behavior of a specific target sorbate when bisorbates are present. Solute competition for sorption sites decreases with increasing rubberyness of an OM matrix. The effect of the increasing rubberyness on the heterogeneity of the sorption process is most pronounced in the case of charcoal, for which the value of *n* increases from 0.21 for single-solute contaminants sorption to 0.49 in the presence of a co-solute. This is consistent with the idea that the high energy sorption sites that exist in an OM are less readily accessible in the glassy state of that SOM than in its rubbery state. More of the high energy sites are made available by matrix swelling and disordering, which can be induced by higher sorbate mass loading ratios that are usually attributed to high residual solution phase concentrations (Weber et al., 2002). Therefore contaminants compete for specific sites in the OM matrix that can bind chlorinated

organic compounds (Xing and Pignatello 1997**)**. Competition occurs in the hole-filling process (Schaefer et al., 2000); the magnitude of the competitive effect likely depends on the extent of overlap between the hole-filling domains, and not in the dissolution domain. Therefore competition is less in peat.

Table 9: Polanyi-Manes model sorption parameters (i) for a single compound on a sorbent (ii) sorption of the compound in a binary sorption system with a corresponding contaminant**.**

sorbent	sorptive [single]	V_0 [cm^3/kg]	E_0 [kJ/mol]	Kp [L/kg]	sorptive [binary]	V_0 [cm^3/kg]	E_0 [kJ/mol]	K_p [L/kg]
Activated carbon	**TCE**	322	13.6	0	**TCE**	200	10.6	0
	PCE	334	9,9	0	**PCE**	260	9	0
	o-xylene	335	13.1	0	**o-xylene**	270	8.8	0
	p-xylene	332	13.5	0	**p-xylene**	270	10.4	0
charcoal	**TCE**	123	15.6	0	**TCE**	102	12.1	0
	PCE	125	12.4	0	**PCE**	105	9.9	0
	o-xylene	135	13.4	0	**o-xylene**	105	10.2	0
	p-xylene	121	14.9	0	**p-xylene**	109	11.9	0
peat	**TCE**	0.22	11.5	9.13	**TCE**	0.21	9.9	11.1
	PCE	0.23	8.1	48.53	**PCE**	0.21	7.3	45.7
	o-xylene	0.22	8.9	32.77	**o-xylene**	0.15	8.9	30.1
	p-xylene	0.23	9.9	33.77	**p-xylene**	0.21	9.4	31.8
zeolite	**TCE**	205	6.6	0	**TCE**	200	6	0
	PCE	192	5.7	0	**PCE**	195	4.9	0
	o-xylene	205	6.0	0	**o-xylene**	200	5.63	0
	p-xylene	204	6.1	0	**p-xylene**	170	5.1	0

Xiao and Huang (2011) showed that adsorption into porous matrix having pore diameters of sizes of the sorbents may generate competition between two sorbents of different sizes due to a size-exclusion or pore-blocking mechanism. This mechanism is mainly important when the pores are irregular and tortuous.

Competitive sorption on activated carbon was shown by Sorial et al. (1993); Lu and Sorial (2004); Lu and Pignatello (2004)) and for charcoal by Sander and Pignatello (2005); Wang et al. (2006), and Yang et al. (2006).

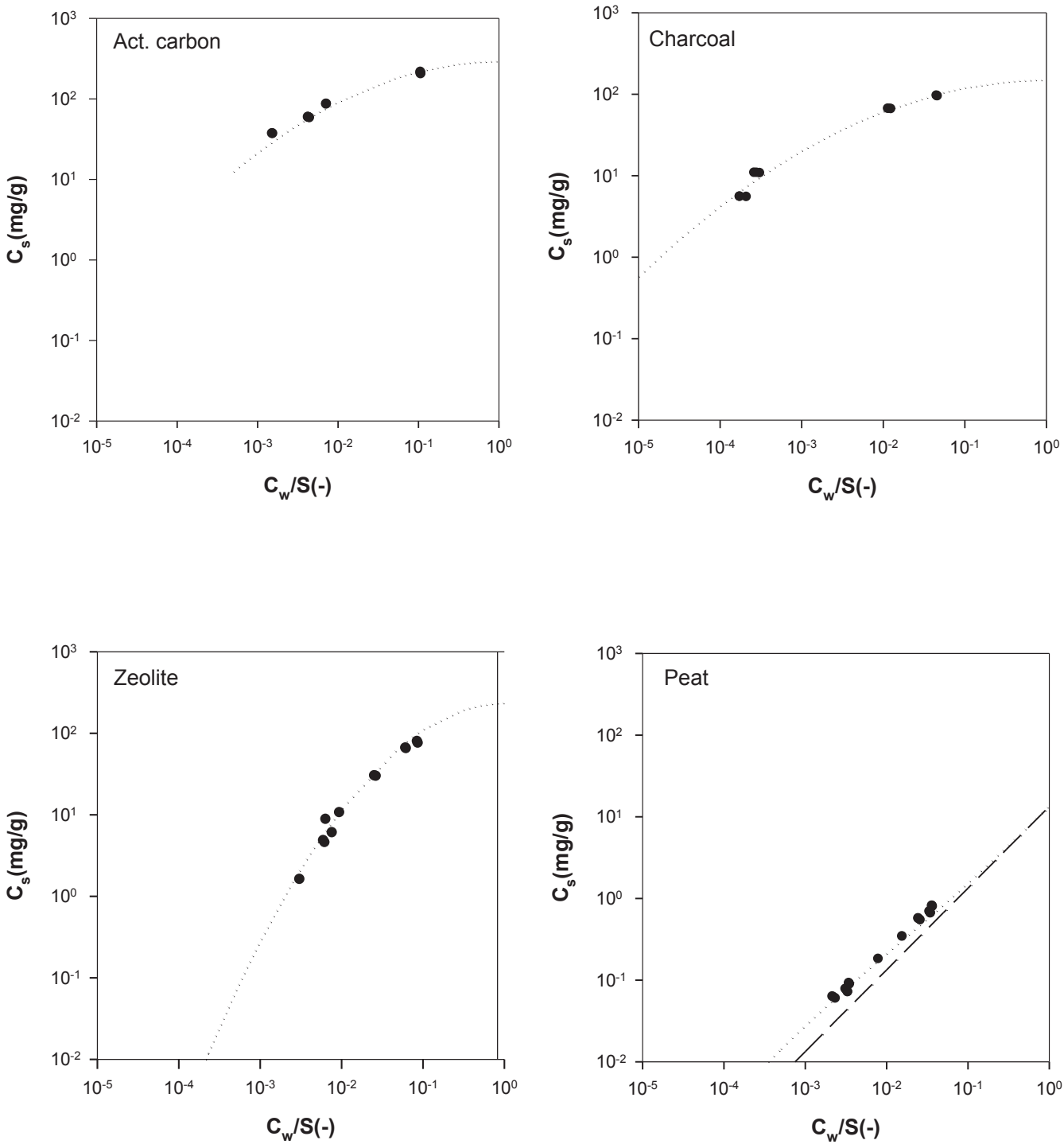


Fig.17: Combined pore-filling and partitioning sorption isotherms of binary TCE
dotted line pore-filling part; dashed line, partitioning part.

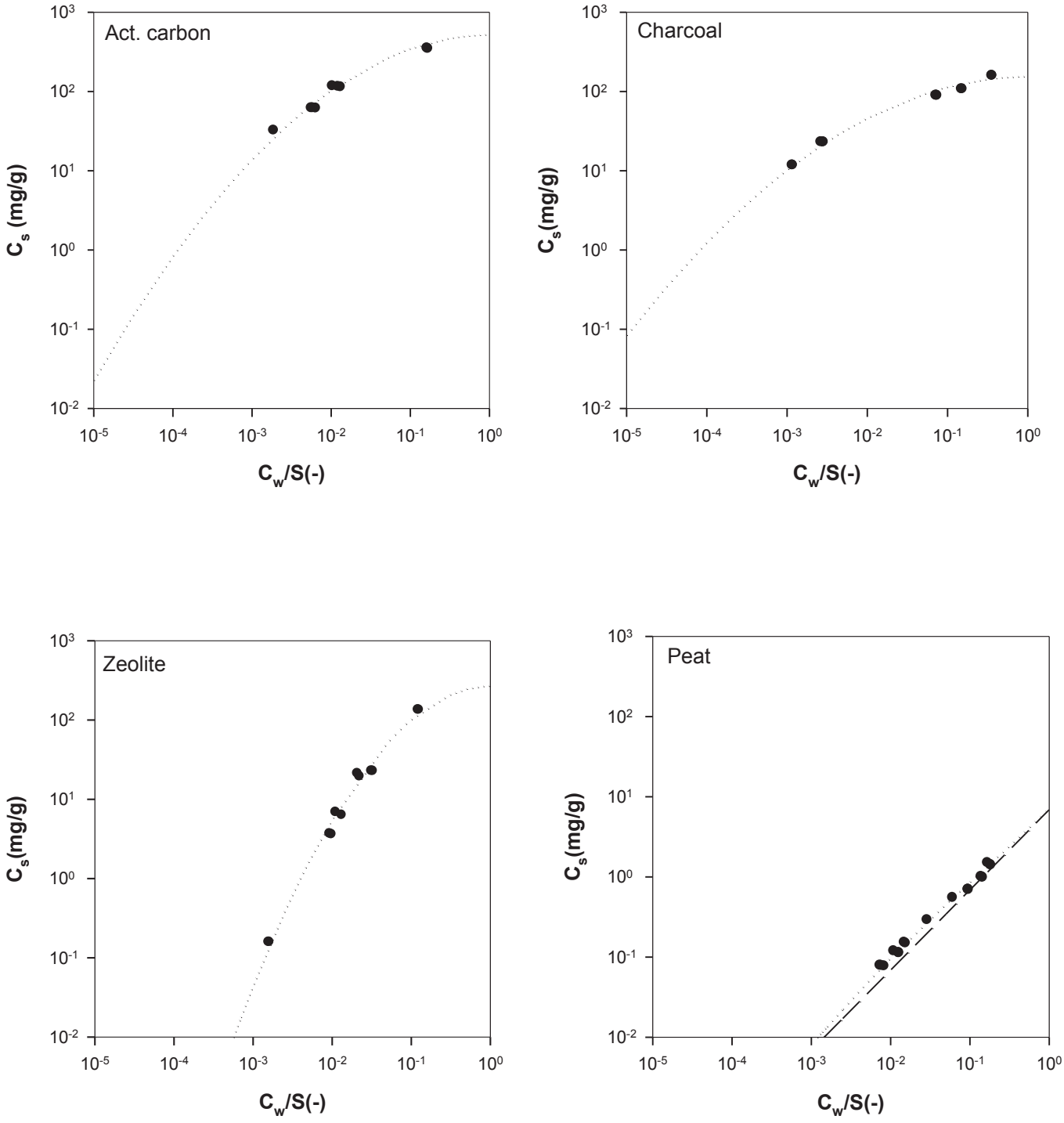


Fig.18: Combined pore-filling and partitioning sorption isotherms of binary PCE
dotted line, pore-filling part; dashed line, partitioning part.

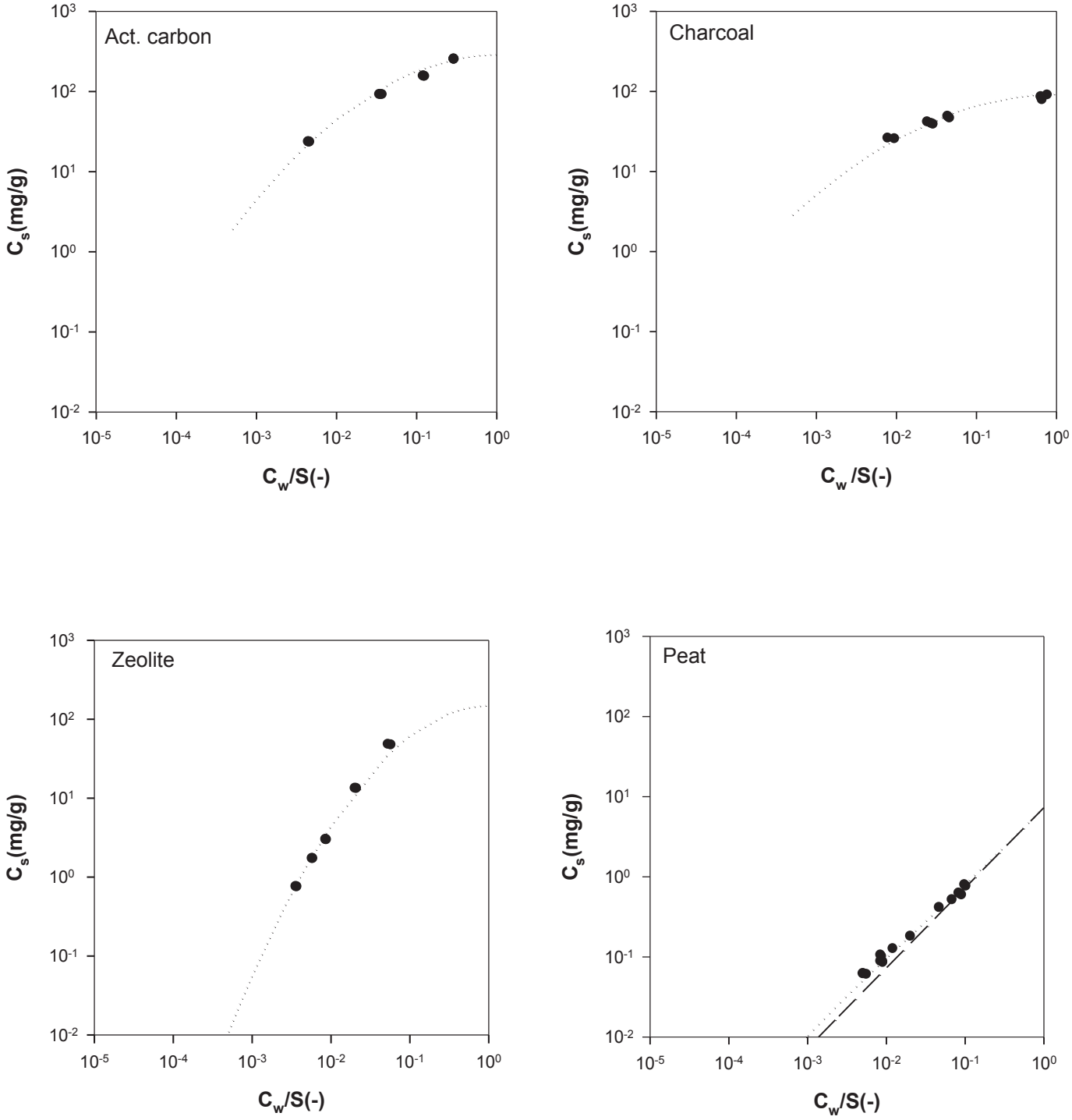


Fig.19: Combined pore-filling and partitioning sorption isotherms of binary o-xylene dotted line, pore-filling part; dashed line, partitioning part.

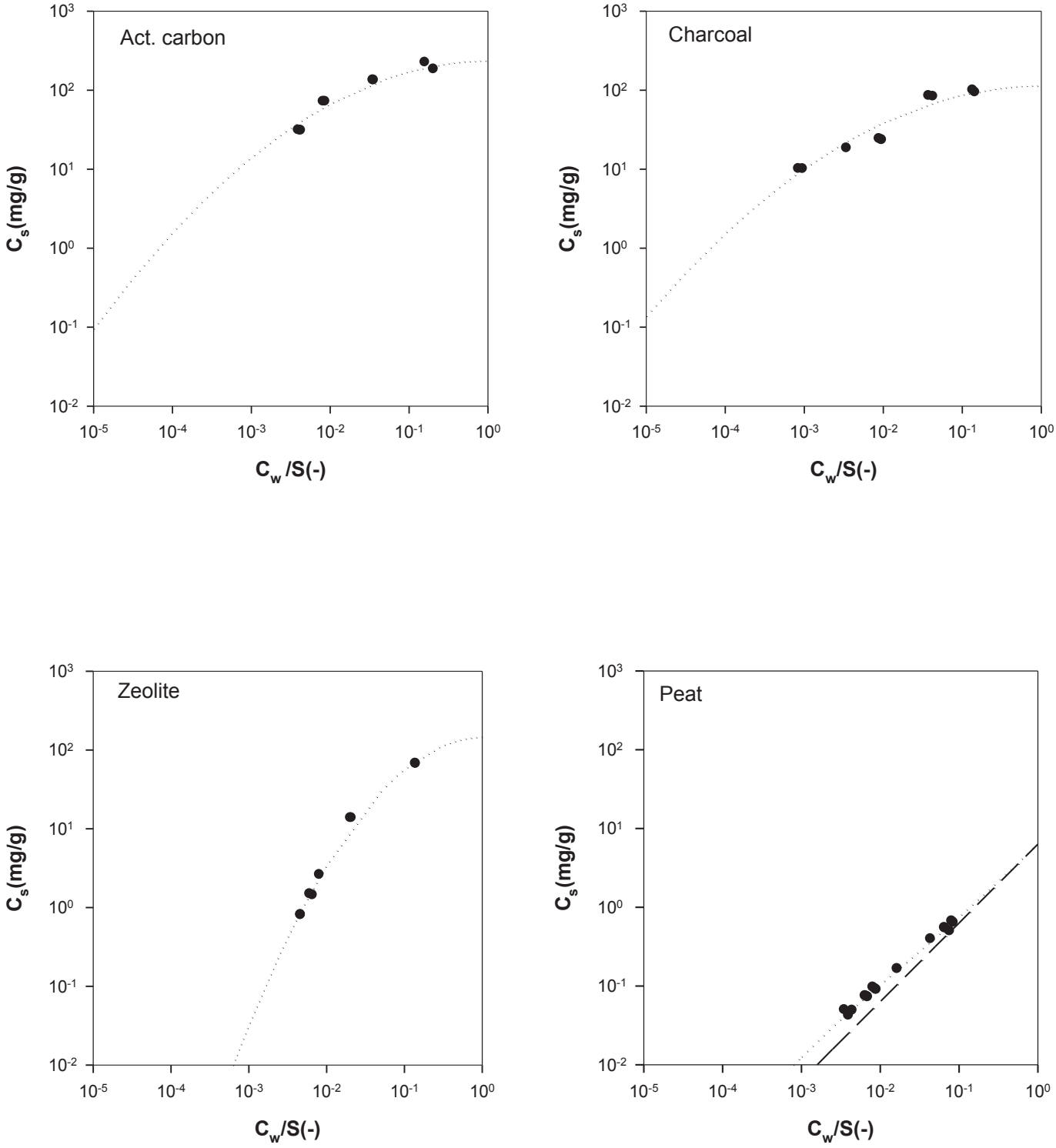


Fig. 20: Combined pore-filling and partitioning sorption isotherms of binary p-xylene dotted line, pore-filling part; dashed line, partitioning part.

It was shown that V_0 (maximum volume of sorbed chemical per unit mass of sorbent) was increasing for the binary system. This may be due to the sorbent matrix bearing pores, the sizes of which may increase after loading of the first sorbent, especially when the first sorbent reaches a relative high concentration inside the space of pores (LeBoeuf and Weber, 2000). In other words, it is suggested that the swelling of OM matrixes in the presence of high concentrations of organic sorbate occur and sorption energy is increased, leading to increased disordering of OM structure. After the sorbent matrix is relaxed and the pore opening increases, the pore that was not accessible before can now be accessed by the larger sorptive. It is possible that the sorption sites in the deformed or expanded pores created by the smaller molecules are high energy sites that are preferentially occupied by the stronger and larger sorptive (Xiao and Huang 2011). Irreversible expansion of holes and irreversible sorption process occurs.

5.2. Second sorption

Results for second sorption after desorption of the corresponding compound for activated carbon, charcoal and zeolite in comparison with the results of the experiments with a single compound are shown in Table 9 (Freundlich parameter) and Table 11 (Polanyi-Manes model Parameter) as well as in comparison with the results of the experiments with a binary solution are listed in Table 10 (Freundlich parameter) and Table 12 (Polanyi-Manes model parameter).

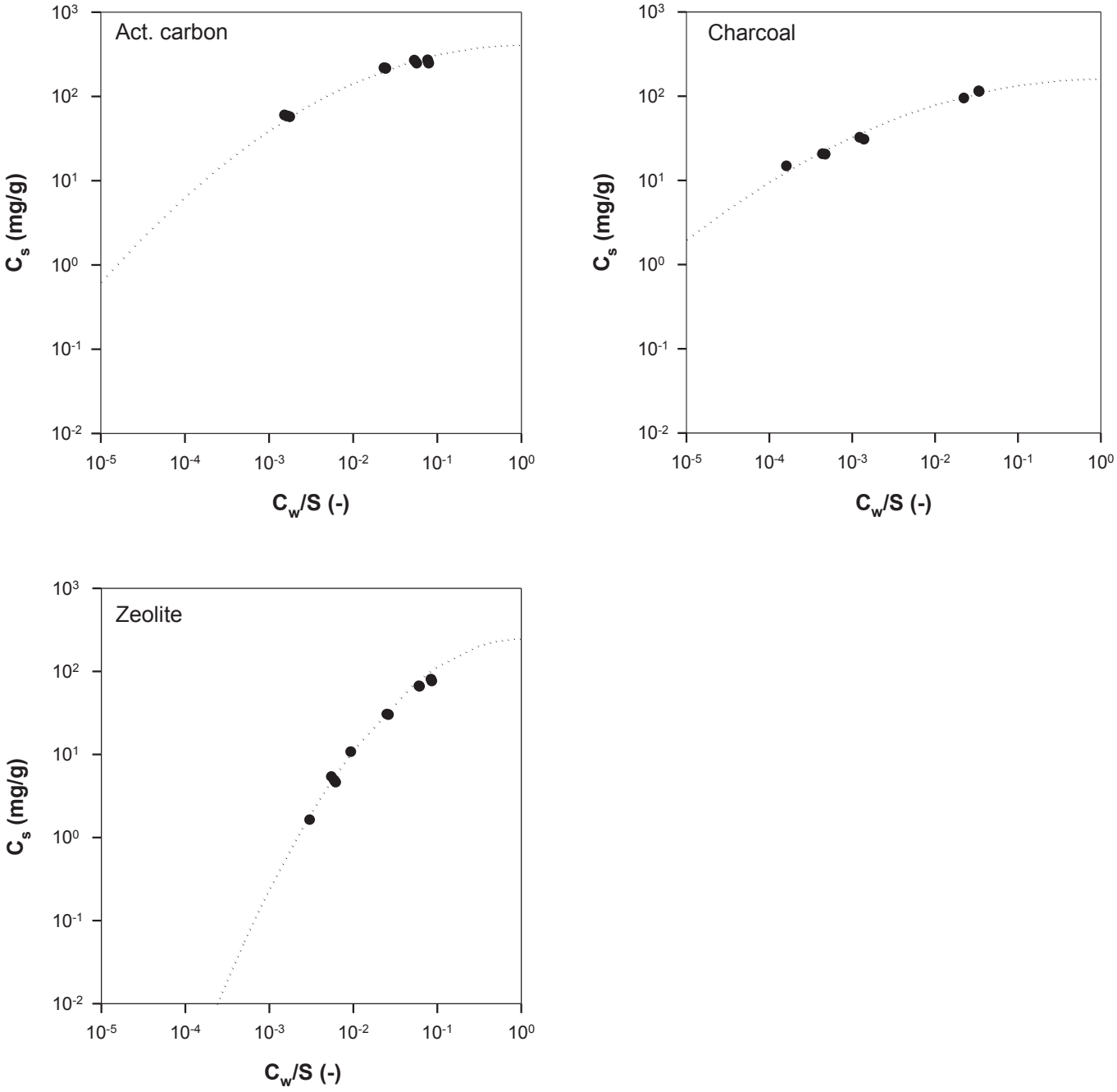


Fig. 21: Sorption of second sorption of TCE on activated carbon, charcoal and zeolite Y-200 and the fitted Polanyi Manes isotherms. Dotted line indicates pore filling part.

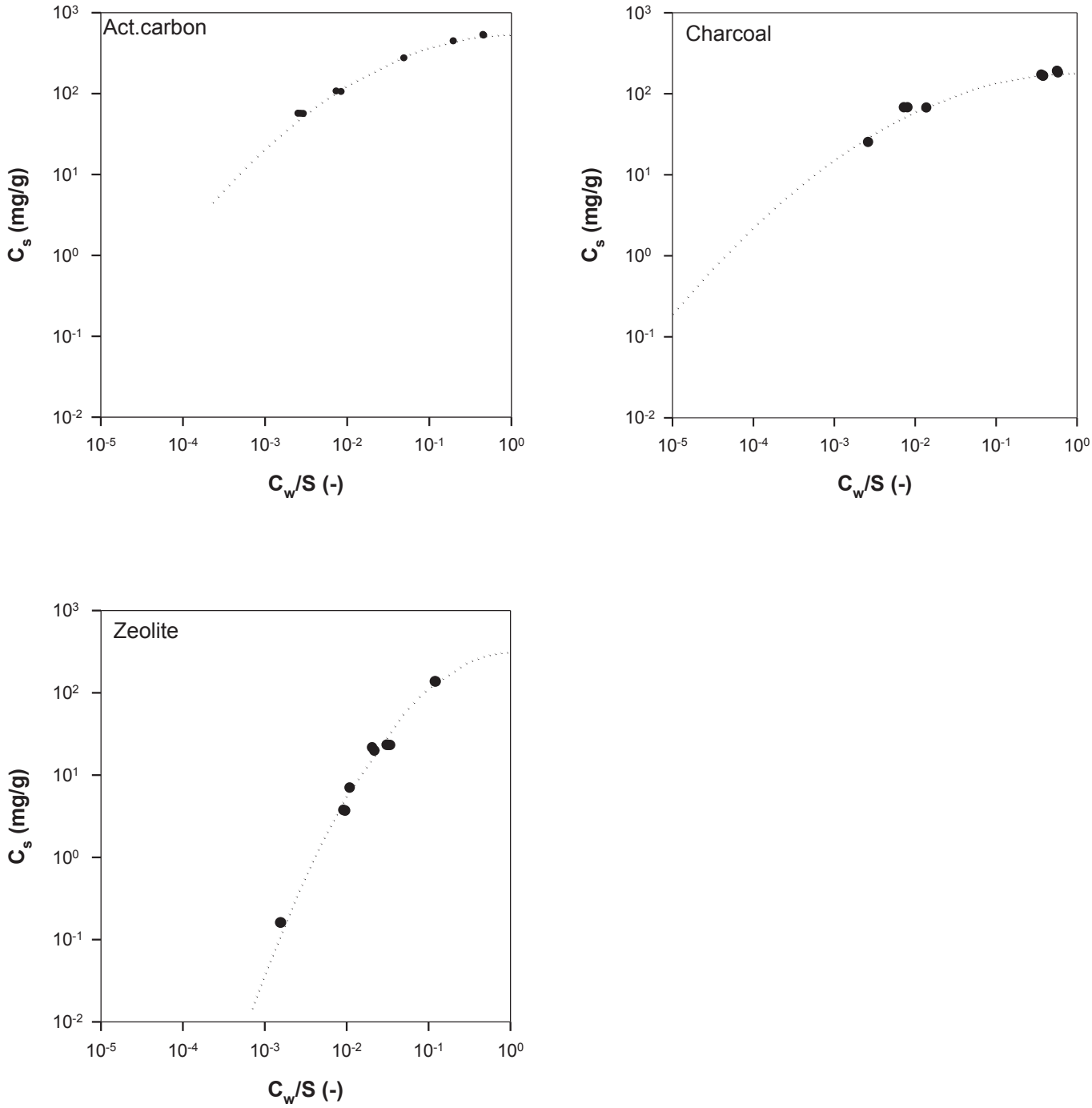


Fig. 22: Sorption of second sorption of PCE on activated carbon, charcoal and zeolite Y-200 and the fitted Polanyi Manes isotherms. Dotted line indicates pore filling part.

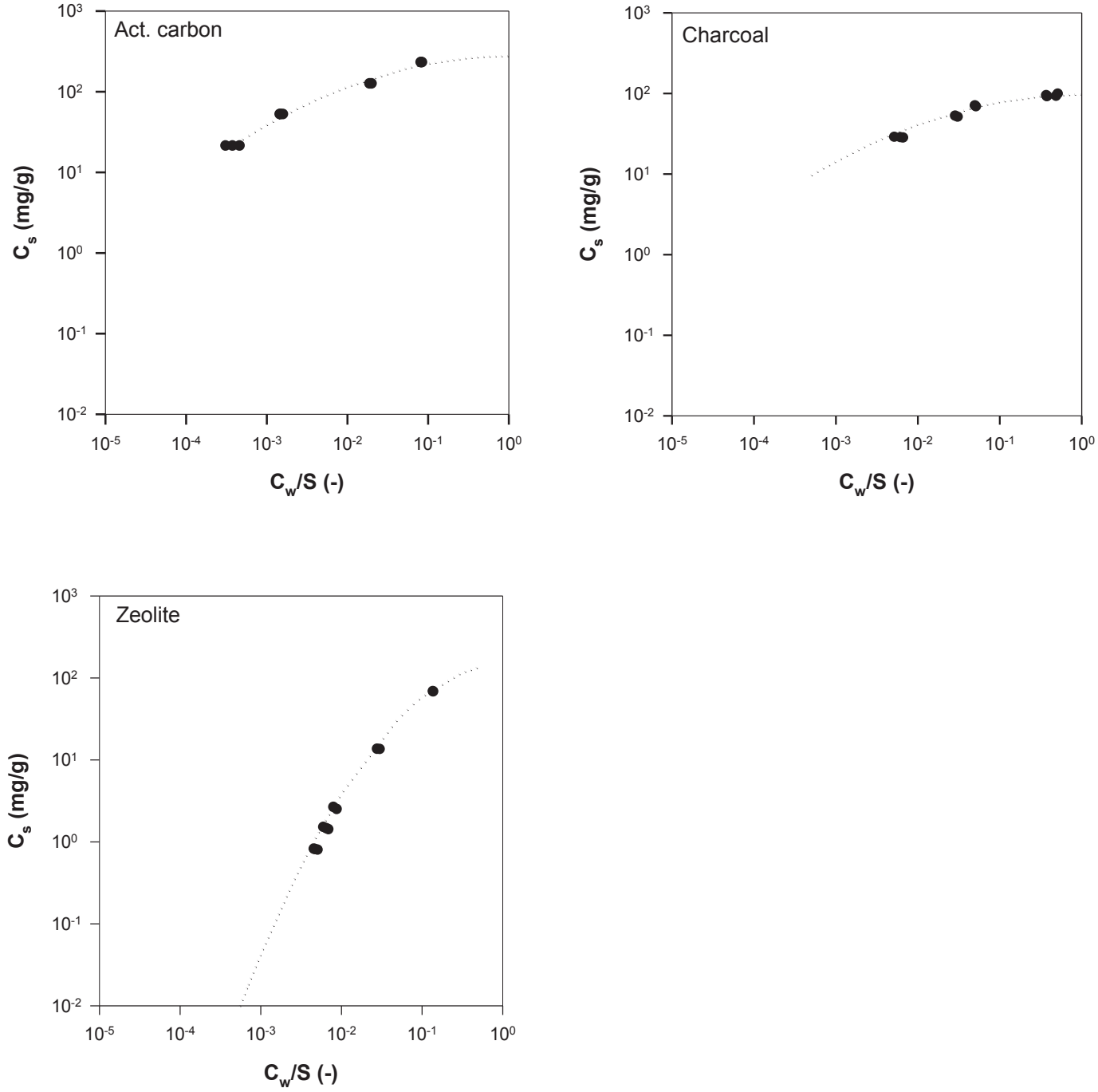


Fig. 23: Sorption of second sorption of o-xylene on activated carbon, charcoal and zeolite Y-200 and the fitted Polanyi Manes isotherms. Dotted line indicates pore filling part.

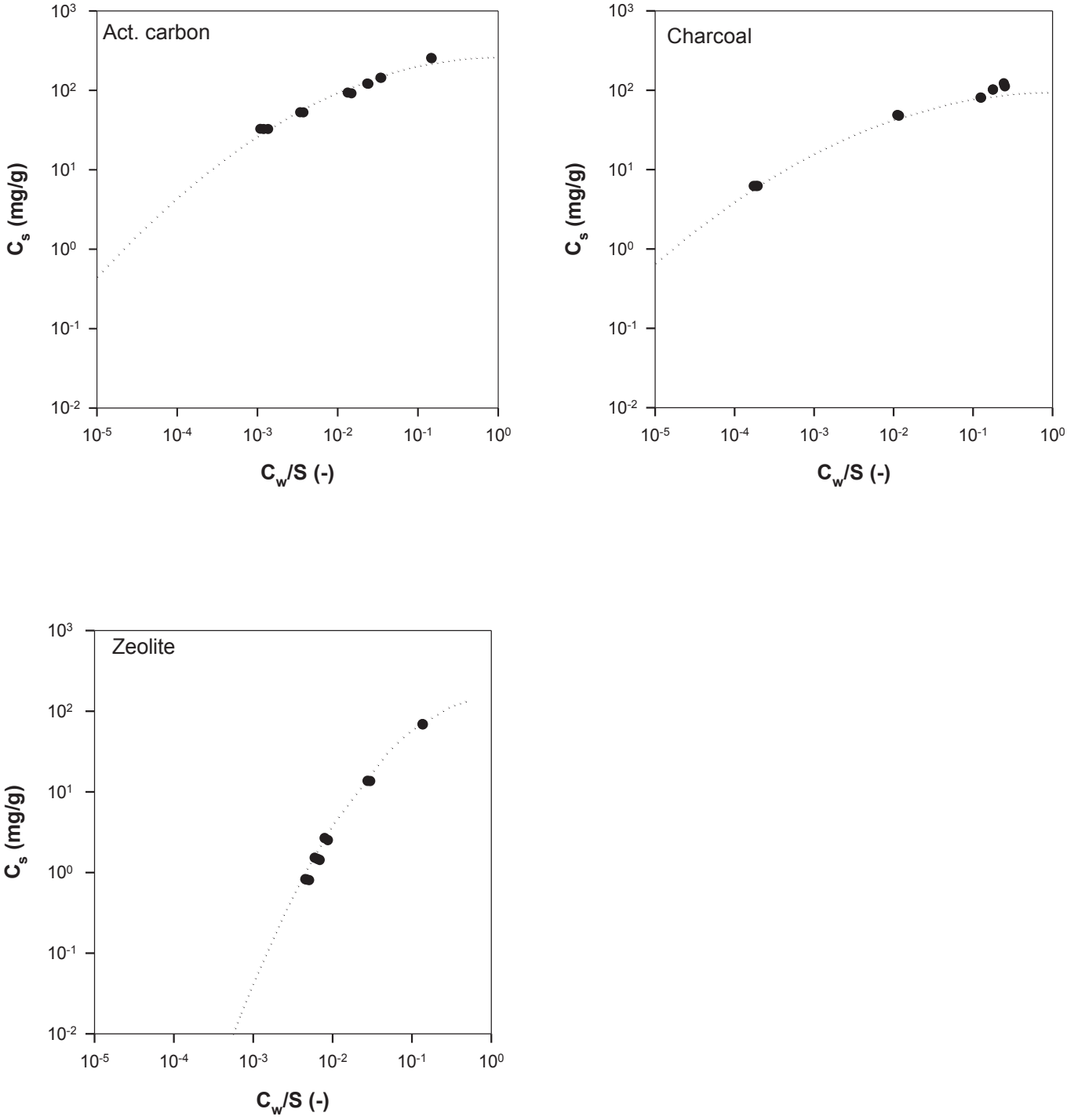


Fig. 24: Sorption of second sorption of p-xylene on activated carbon, charcoal and zeolite Y-200 and the fitted Polanyi Manes isotherms. Dottedline indicates pore filling part.

5.3. Comparison of first and second sorption

The results for the second sorption of one compound after desorption of the corresponding compound for activated carbon, charcoal and zeolite are presented in Figure 29 and 30 for PCE and o-Xylene respectively, in comparison to the first sorption step of the single compound.

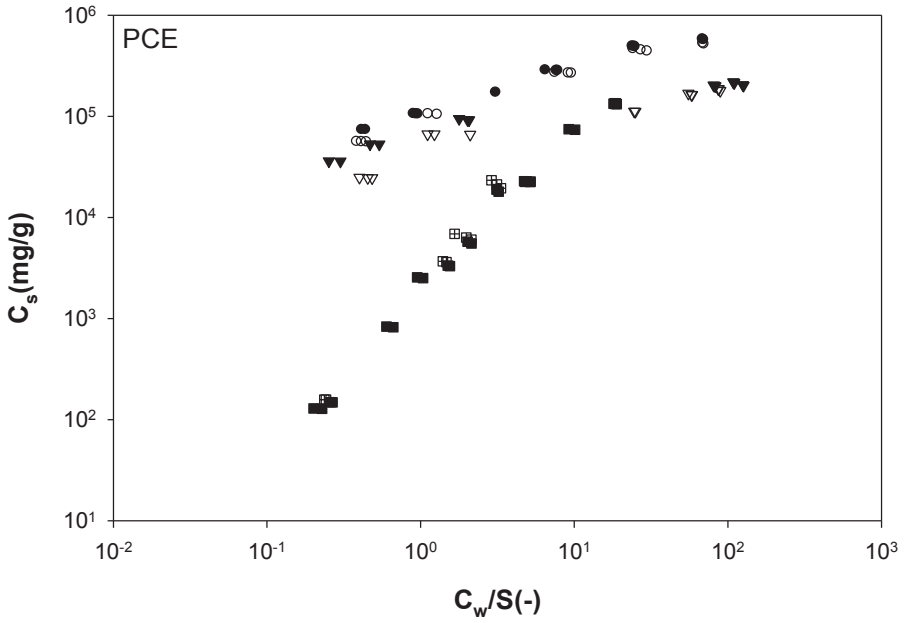


Fig. 25: Comparison of the first sorption isotherms (full symbols) with the second sorption isotherm (open symbols) after desorption of TCE on activated carbon (circles), charcoal (triangles), and zeolite Y-200 (squares).

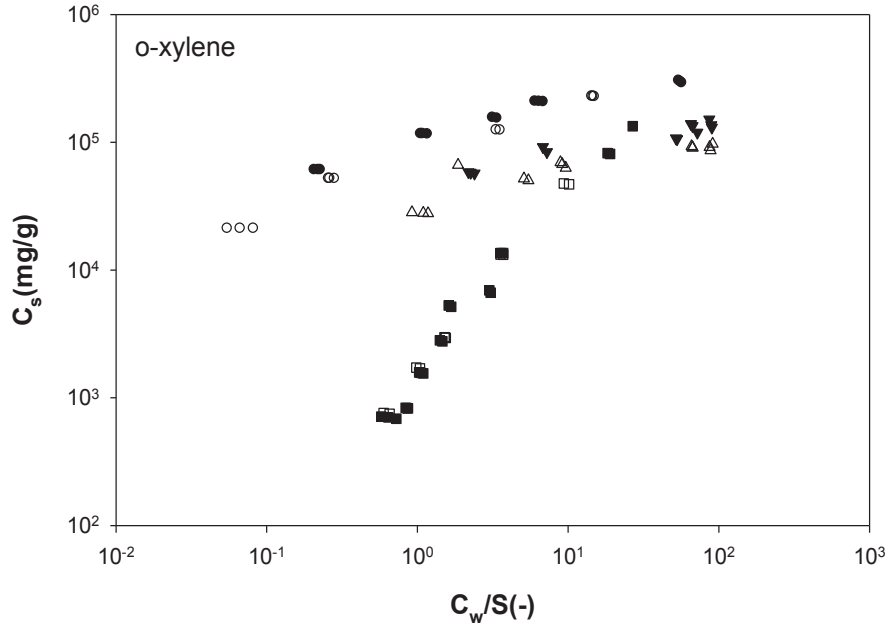


Fig.26: Comparison of the first sorption isotherms (full symbols) with the second sorption isotherm (open symbols) after desorption of o-Xylene on activated carbon (circles), charcoal (triangles), and zeolite Y-200 (squares).

in comparison with the results of the experiments with a single compound are shown in Table 9 (Freundlich parameter) and Table 11 (Polanyi-Manes model Parameter) as well as in comparison with the results of the experiments with a binary solution are listed in Table 10 (Freundlich parameter) and Table 12 (Polanyi-Manes model Parameter).

Table 10: Freundlich sorption parameters (i) for a single compound on a sorbent (ii) sorption of the compound after desorption of the corresponding sorptive.

sorbent	**sorptive Single**	**K_f [L/kg]**	**1/n [-]**	**sorptive after desorption**	**k_f [L/kg]**	**1/n [-]**
Activated carbon	**TCE**	70820	0.39	**TCE**	45570	0.4
	PCE	11055	0.43	**PCE**	90610	0.45
	o-xylene	10543	0.28	**o-xylene**	75300	0.42
	p-xylene	80690	0.38	**p-xylene**	59010	0.43
charcoal	**TCE**	42690	0.28	**TCE**	26770	0.39
	PCE	63030	0.26	**PCE**	41880	0.33
	o-xylene	50620	0.21	**o-xylene**	31120	0.26
	p-xylene	38390	0.28	**p-xylene**	24820	0.39
zeolite	**TCE**	560	1.14	**TCE**	680	1.05
	PCE	1740	1.66	**PCE**	2014	1.56
	o-xylene	1460	1.43	**o-xylene**	1610	1.51
	p-xylene	1880	1.24	**p-xylene**	1020	1.131

Table 11: Freundlich sorption parameters (i) sorption of the compound in a binary sorption system with a corresponding contaminant (ii) sorption of the compound after desorption of the corresponding sorptive (Freundlich parameter)

sorbent	**sorptive in a binary system**	**Kf [L/kg]**	**1/n [-]**	**sorptive after desorption**	**kf [L/kg]**	**1/n [-]**
Activated carbon	**TCE**	31760	0.37	**TCE**	45570	0.4
	PCE	70370	0.47	**PCE**	90610	0.45
	o-xylene	28070	0.56	**o-xylene**	75300	0.42
	p-xylene	42500	0.48	**p-xylene**	59010	0.43
charcoal	**TCE**	14490	0.49	**TCE**	26770	0.39
	PCE	27710	0.41	**PCE**	41880	0.33
	o-xylene	25290	0.27	**o-xylene**	31120	0.26
	p-xylene	21830	0.48	**p-xylene**	24820	0.39
zeolite	**TCE**	143	1.43	**TCE**	680	1.05
	PCE	290	2.42	**PCE**	2014	1.56
	o-xylene	147	1.41	**o-xylene**	1610	1.51
	p-xylene	270	1.61	**p-xylene**	1020	1.131

Results show that the sorption capacity of second sorption is less than the first sorption. This may be due to that not all energetically favored sites are available for sorption. Some of them may also already be occupied.

Table 12: Polanyi-Manes model sorption parameters (i) for a single compound on a sorbent (ii) sorption of the compound after desorption of the corresponding sorptive.

sorbent	**sorptive [single]**	**V_0 [cm^3/kg]**	**E_0 [kJ/mol]**	**K_p [L/kg]**	**sorptive after desorption**	**V_0 [cm^3/kg]**	**E_0 [kJ/mol]**	**K_p [L/kg]**
Activated carbon	**TCE**	322	13.6	0	**TCE**	280	11.2	0
	PCE	334	9.9	0	**PCE**	326	9.5	0
	o-xylene	335	13.1	0	**o-xylene**	315	12.2	0
	p-xylene	332	13.5	0	**p-xylene**	305	11.3	0
charcoal	**TCE**	123	15.6	0	**TCE**	110	13.6	0
	PCE	125	12.4	0	**PCE**	110	10.9	0
	o-xylene	135	13.4	0	**o-xylene**	110	12.4	0
	p-xylene	121	14.9	0	**p-xylene**	110	12.8	0
zeolite	**TCE**	205	6.6	0	**TCE**	170	6.5	0
	PCE	192	5.7	0	**PCE**	190	5.7	0
	o-xylene	205	6.0	0	**o-xylene**	205	5.9	0
	p-xylene	204	6.1	0	**p-xylene**	170	6	0

Table 13: Sorption parameters of the compound in a binary sorption system with a correspondingcontaminant (ii) sorption of the compound after desorption of the corresponding sorptive (Polanyi-Manes model parameters).

sorbent	sorptive [Binary]	V_0 [cm^3/kg]	E_0 [kJ/mol]	K_p [L/kg]	sorptive after desorption	V_0 [cm^3/kg]	E_0 [kJ/mol]	K_p [L/kg]
Activated carbon	**TCE**	200	10.6	0	**TCE**	280	11.2	0
	PCE	260	9	0	**PCE**	326	9.5	0
	o-xylene	270	8.8	0	**o-xylene**	315	12.2	0
	p-xylene	270	10.4	0	**p-xylene**	305	11.3	0
charcoal	**TCE**	102	12.1	0	**TCE**	110	13.6	0
	PCE	105	9.9	0	**PCE**	110	10.9	0
	o-xylene	105	10.2	0	**o-xylene**	110	12.4	0
	p-xylene	109	11.9	0	**p-xylene**	110	12.8	0
zeolite	**TCE**	200	6	0	**TCE**	170	6.5	0
	PCE	195	4.9	0	**PCE**	190	5.7	0
	o-xylene	200	5.63	0	**o-xylene**	205	5.9	0
	p-xylene	170	5.1	0	**p-xylene**	170	6	0

K_{oc}-S and K_{oc}-K_{ow} correlations

Distribution coefficients of hydrophobic organic contaminates tend to decrease with increasing water solubility. K_f values were therefore calculated at 10 % of the compounds water solubility from experimental data. The results show an inverse relation between the water solubility and the K_f values: The K_f values decrease with increasing solubility of a compound and furthermore with increasing organic content the K_f increases. When the k_f values are plotted versus 10 % of solubility the slope is -0.6 to -0.76 (Fig. 27) which is similar to what are reported previously (from -0.6 to -0.7).

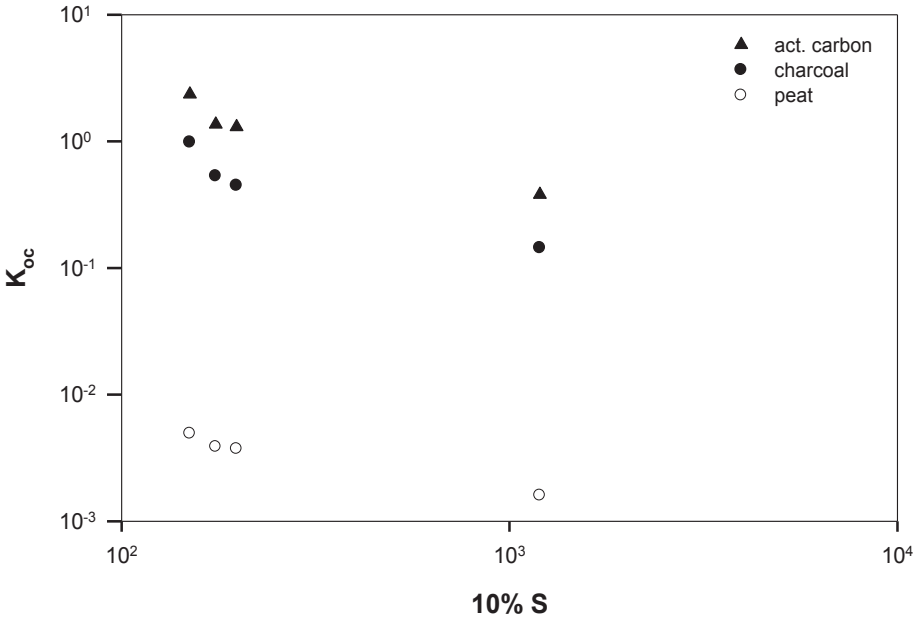
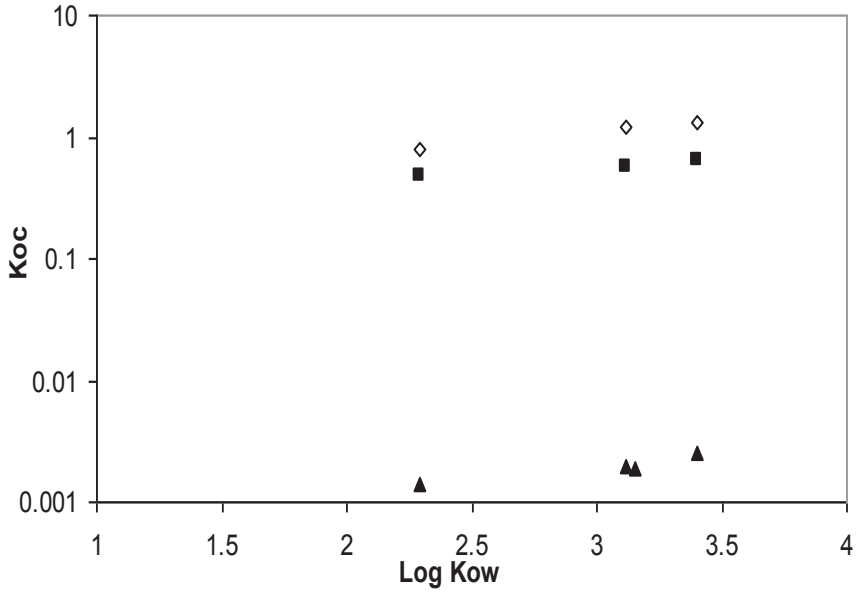


Fig. 27: The relation between the water solubility and K_{oc}.

After normalization the K_{oc} to the organic content of the sorbent, sorption increases with increasing K_{ow} value (Fig. 28) .



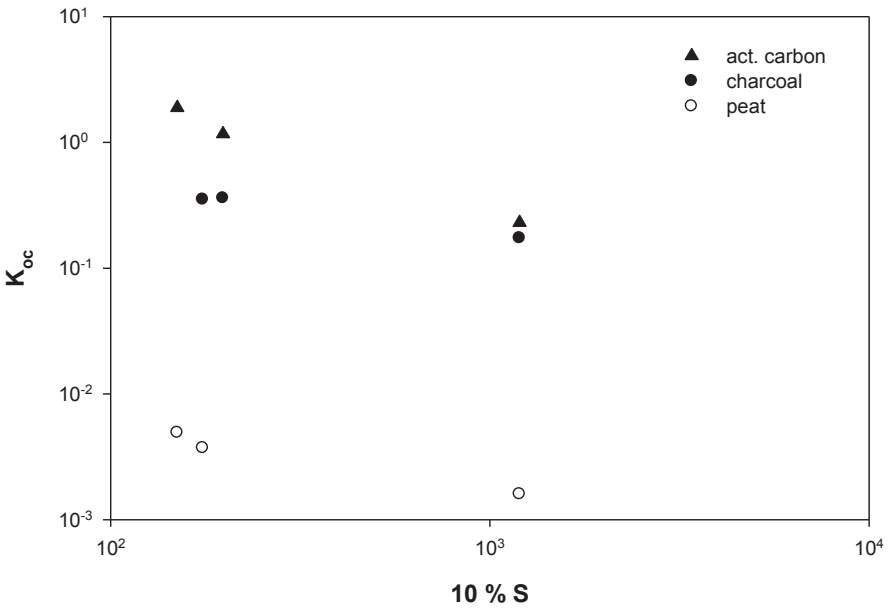


Fig.28: The relation between k_{oc} and Log K_{ow}

5.4 Respiking experiments

After the sorption isotherms were completed the vials were opened and desorbed by bubbling nitrogen through the water phase on a sand bath kept at 40°C. Prior to the second sorption step, the evaporated water was replaced by adding an appropriate amount of deionized water. Then, the complementary compound was spiked to the samples in the same way as the initial compound, e.g. to give again an isotherm, and vials were capped. After 7 days, concentrations of the initial compound and the complementary compound in the aqueous phase were determined by analyzing the gas phase in the headspace of the vials.

The second sorption of the complementary compound causes the initially sorbed compound to desorb. Desorption in principal can be attributed to two possible processes, (i) competition for sorption sites between the two compounds while the complementary compound is present in much higher concentration, and (ii) release of the initial compound due to swelling and reconfiguration of the sorbent as the complementary compound is added in high concentrations.

By analysing the concentration of the initial compound in the water phase and knowing the volume of water in the vials, the released mass of the initial compound can be calculated.

Finally, the vials were opened again and the water replaced by 5 ml of methanol. The vials were recapped and kept on the sand bath at 40°C for final extraction. It is assumed, that this procedure desorbs any compound that is still left on the sorbent. The total desorbed mass of the initially sorbed compound was then calculated by summarizing the amount released during respiking and the amount released due to the final addition of methanol.

5.4.1 Desorption due to respiking and methanol extraction

In the following the isotherms for the different contaminants on activated carbon and charcoal in a single system in comparison to the isotherms for the pollutants in a binary system with the complementary compound are shown. In addition, the isotherms of the corresponding compound after desorption of the initial compound are shown and the corresponding desorbed mass of the initial compound (Fig. 29–Fig. 36).

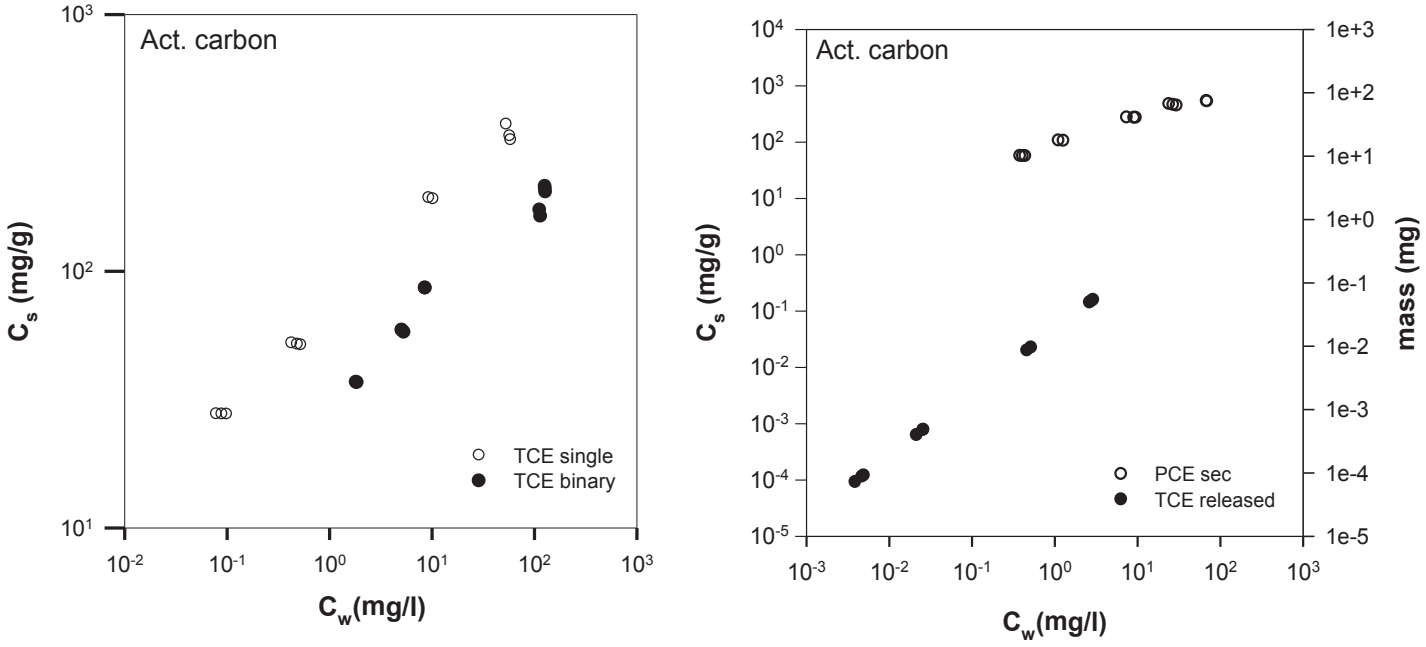


Fig.29: Sorption isotherms of TCE in a single and binary system on activated carbon (left) Sorption isotherm for PCE after desorption of TCE on activated carbon and released TCE (right).

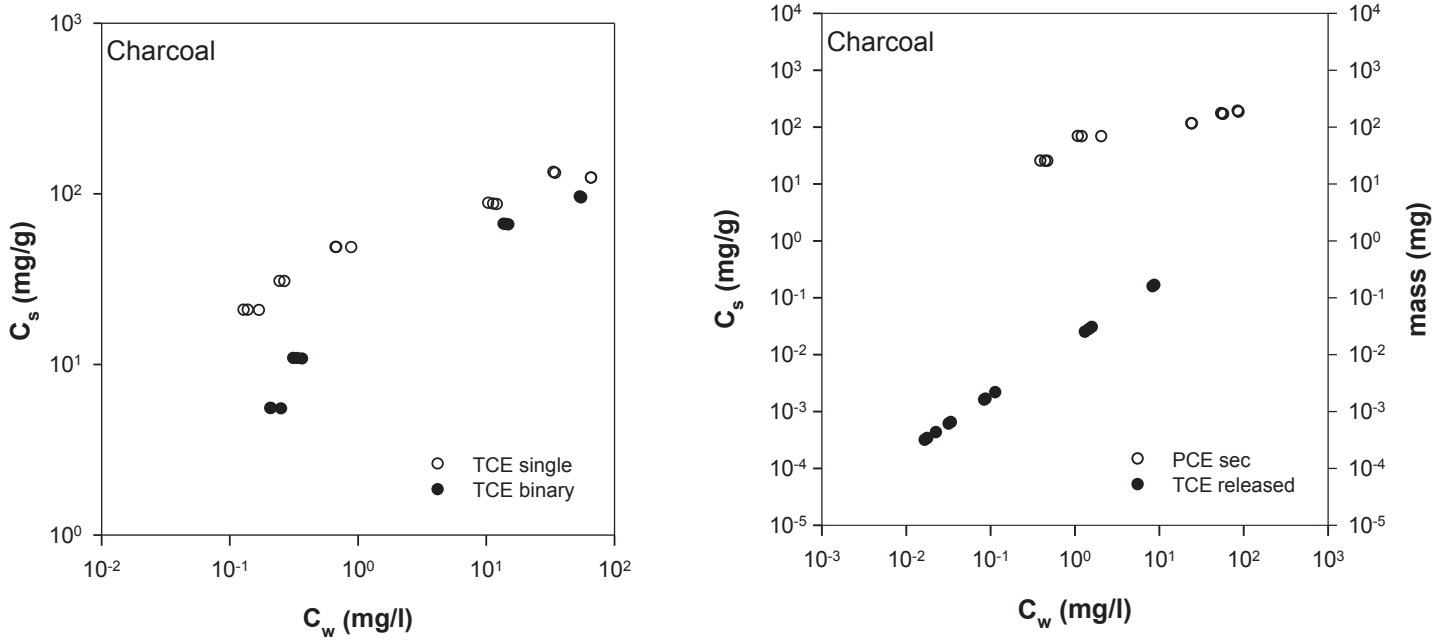
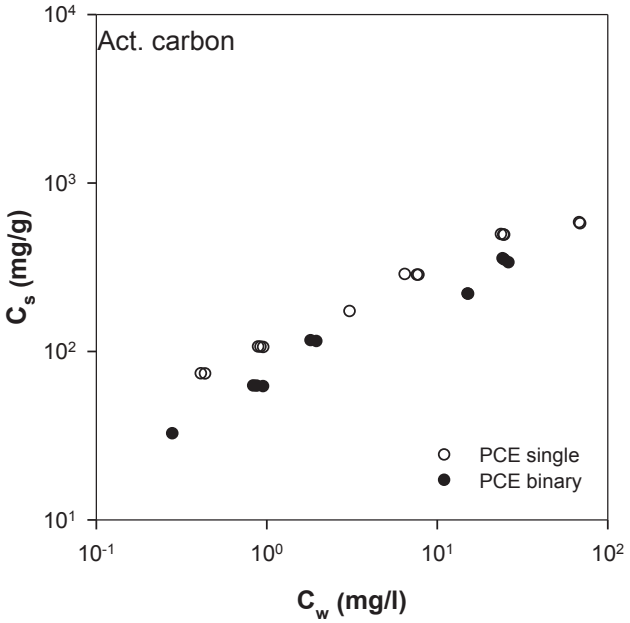


Fig.30: Sorption of TCE as a single compound and in a binary system on charcoal (left) Sorption isotherm for PCE after desorption of TCE on charcoal and released TCE (right).



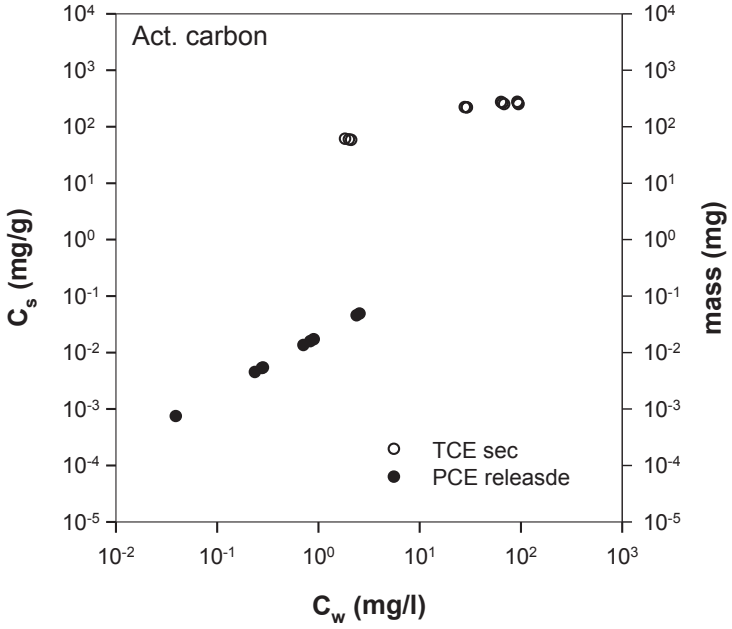
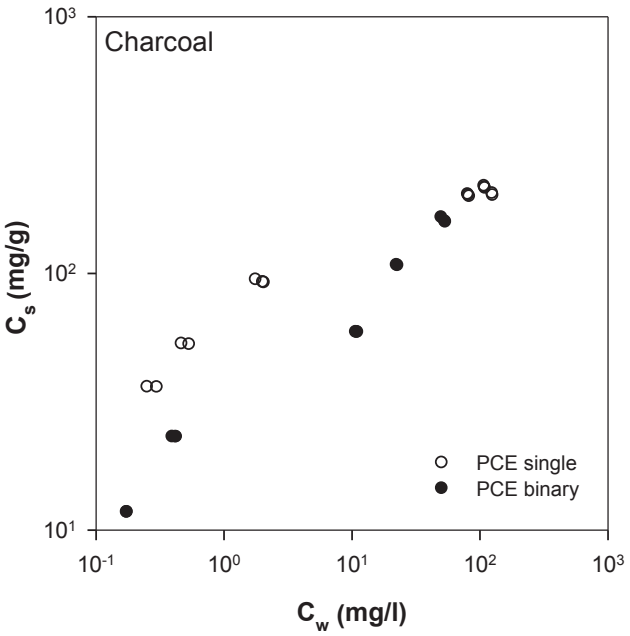


Fig.31: Sorption of PCE as a single compound and in a binary system on activated carbon (left) Sorption isotherm for TCE after desorption of PCE on activated carbon and released PCE (right).



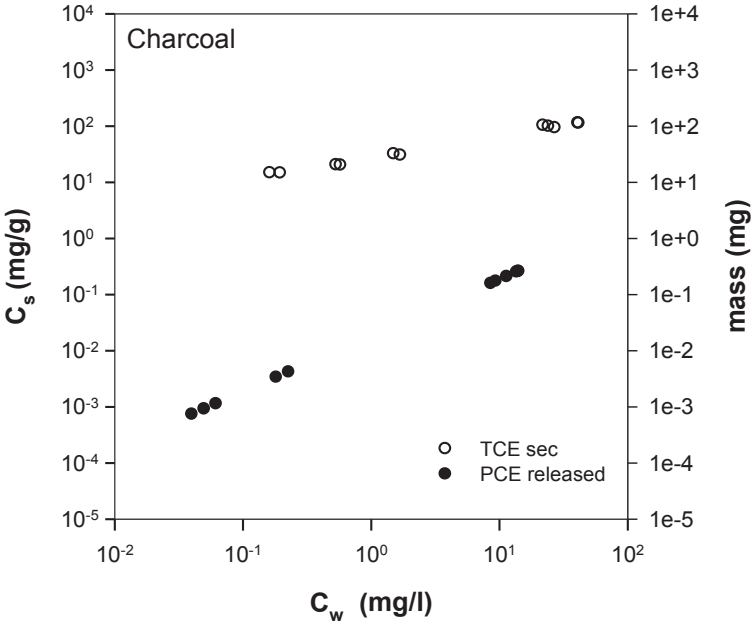


Fig.32: Sorption of PCE as a single compound and in a binary system on charcoal (left). Sorption isotherm for TCE after desorption of PCE on charcoal and released PCE (right).

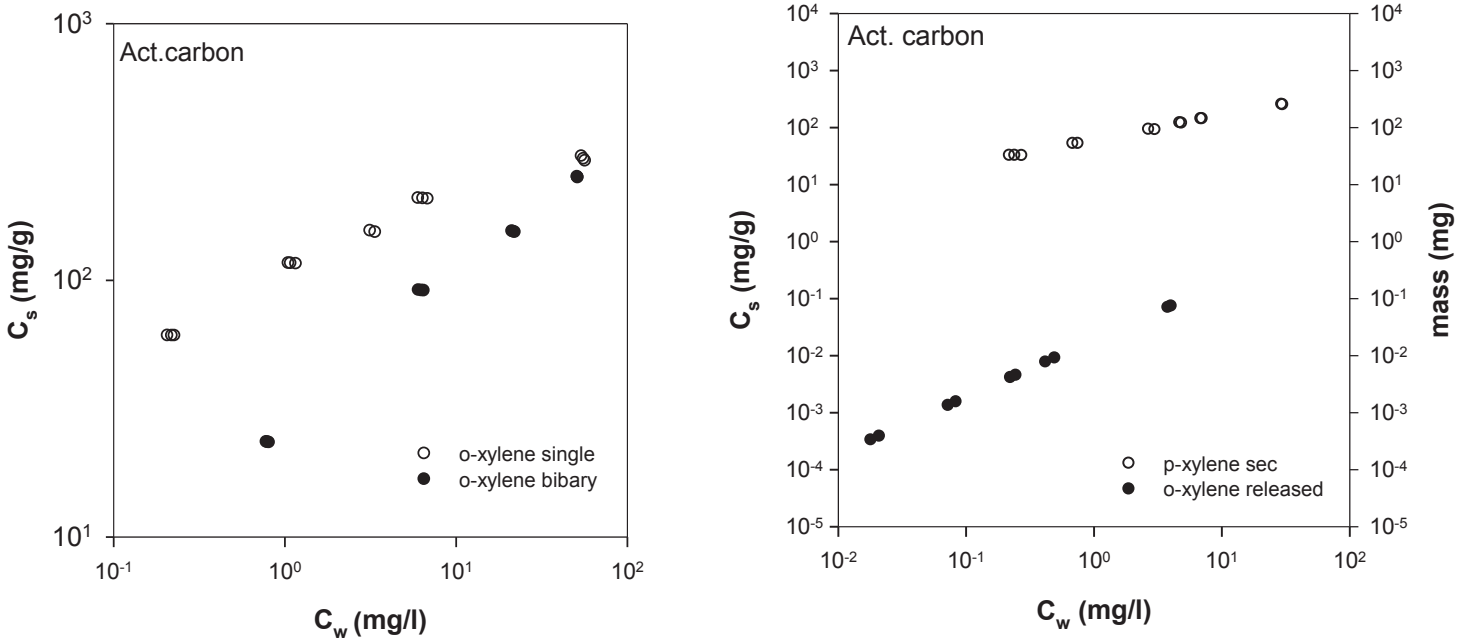


Fig.33: Sorption of o-xylene as a single compound and in a binary system on activated carbon (left). Sorption isotherm for p-xylene after desorption of o-xylene on activated carbon and released o-xylene (right)

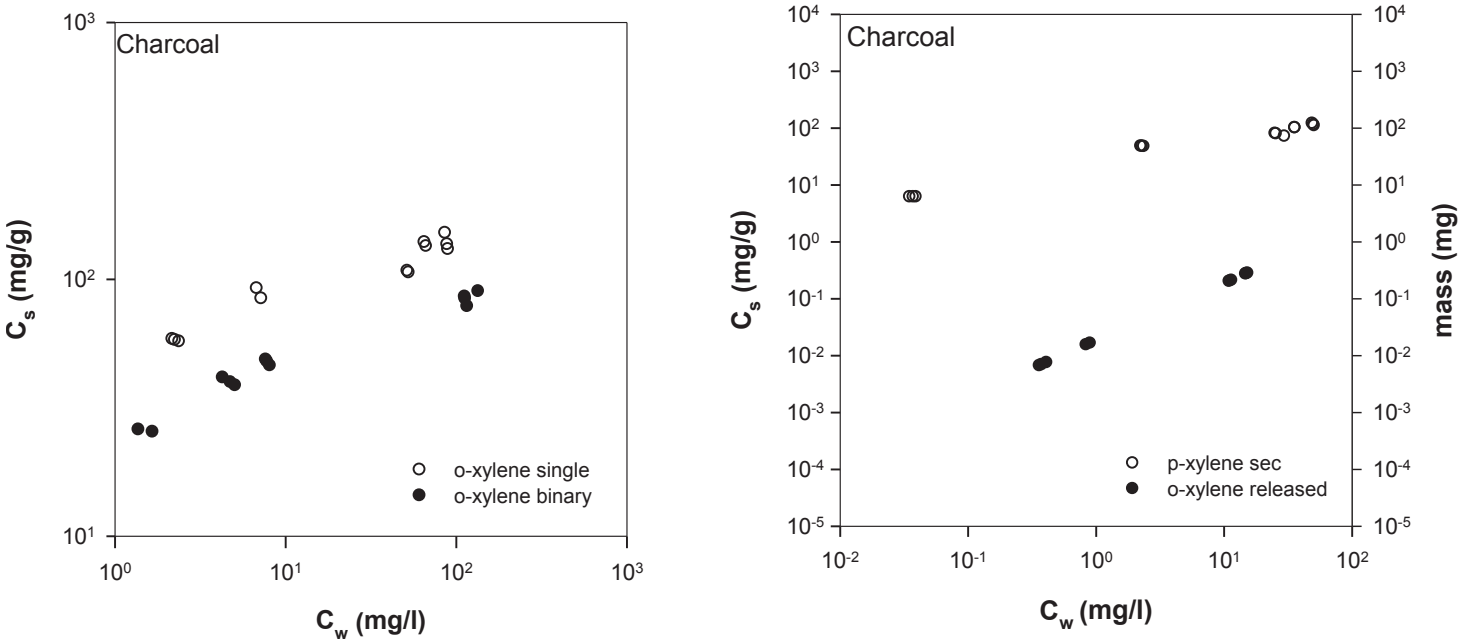


Fig.34: Sorption of o-xylene as a single compound and in a binary system on charcoal (left). Sorption isotherm for p-xylene after desorption of o-xylene on charcoal and released o-xylene (right)

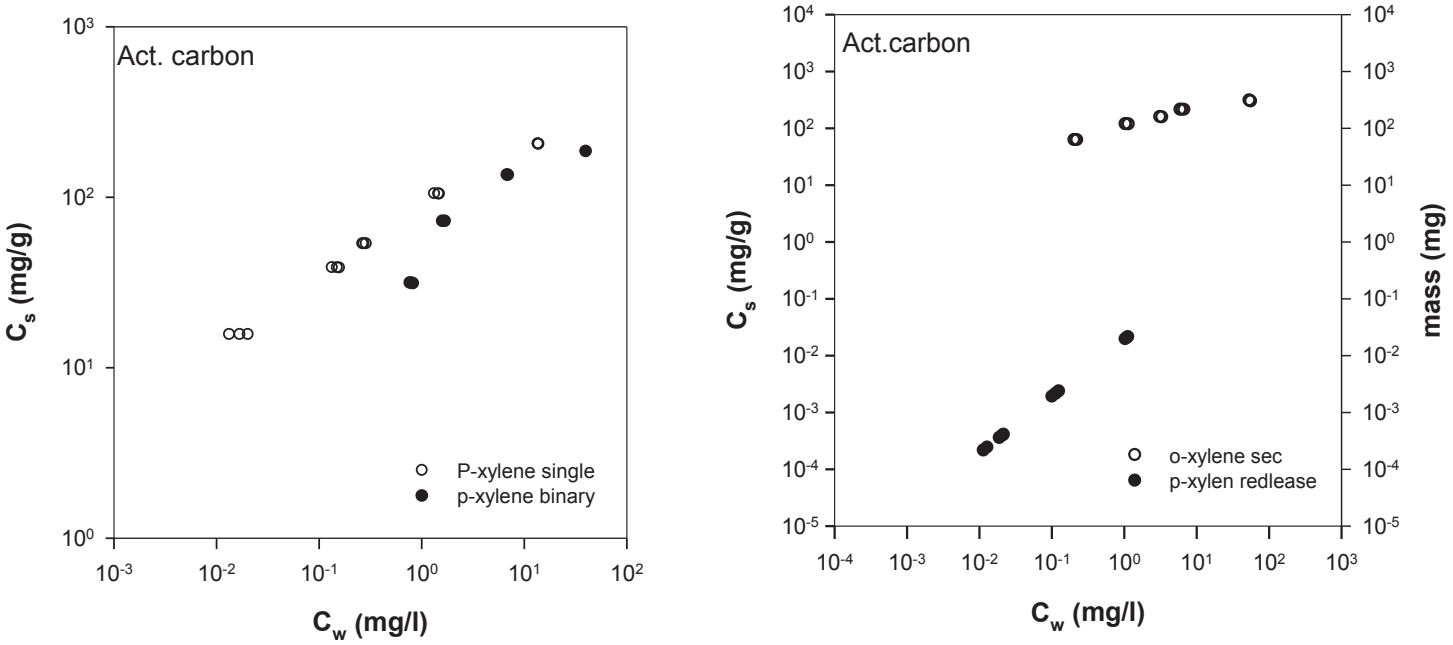


Fig. 35: Sorption of p-xylene as a single compound and in a binary system on activated carbon (left). Sorption isotherm for o-xylene after desorption of p-xylene on activated carbon and released o-xylene (right)

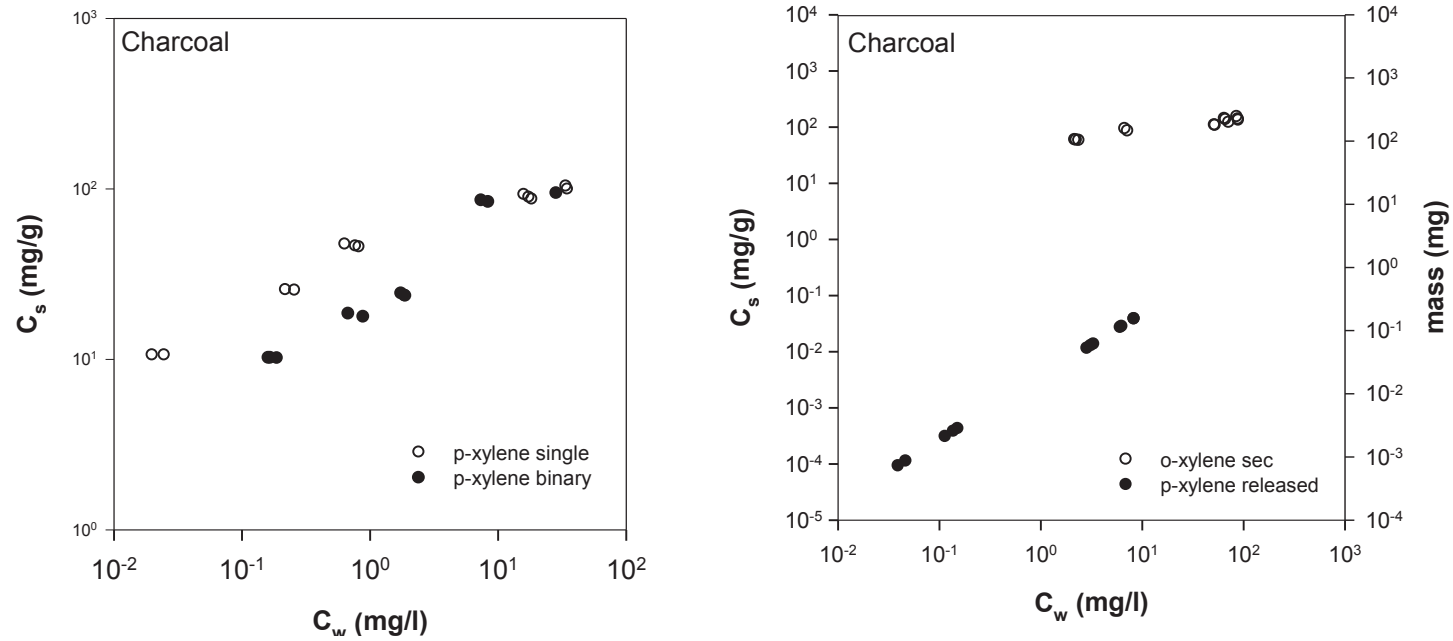


Fig. 36: Sorption of p-xylene as a single compound and in a binary system on charcoal (left). Sorption isotherm for o-xylene after desorption of p-xylene on charcoal and released o-xylene (right).

For the zeolite, no desorption of the initial compound due to the spiking of the complementary compound could be observed, indicating an extensive desorption of the initial compound already in the first desorption step. Isotherms are shown in Fig. 37.

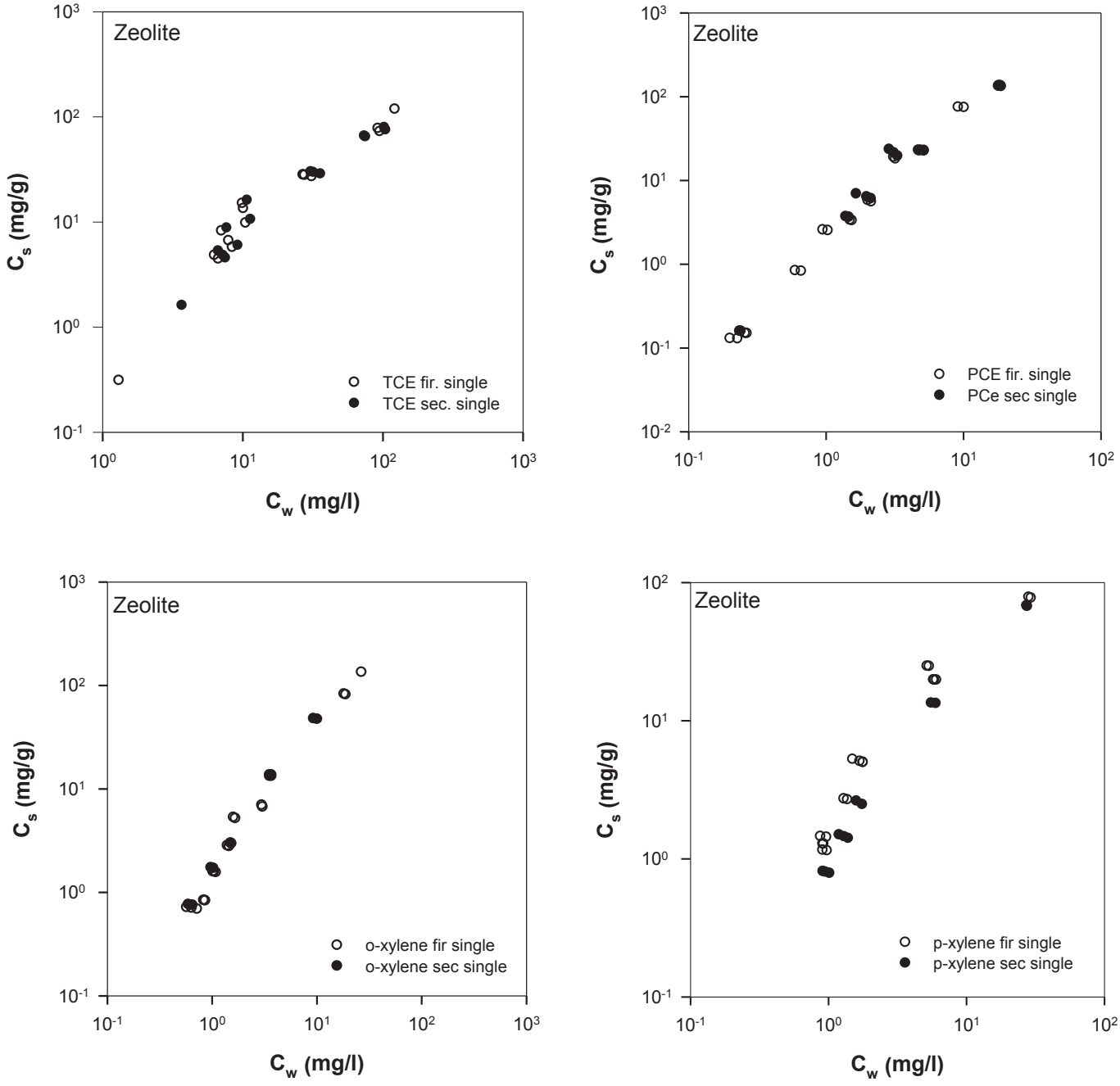


Fig. 37: Sorption isotherms for sorption of a single contaminant and sorption of the same single contaminant after desorption of the respective corresponding compound TCE, PCE, o-xylene and p-xylene.

In the binary system, isotherms were to some extend influenced by the corresponding compound as discussed in chapter 5. However, the isotherm of a compound in the second sorption step after desorption of the initial compound was very similar to the single isotherm of that compound. This is most obvious for the zeolite data (Fig. 41) where the second isotherm of a compound, after desorption of the initial compound, collapses on the first single isotherm. This again indicates that for the zeolite with its rigid pore structure no significant hysteresis occurs.

For the charcoal and the activated carbon, significant amounts of the initial compound were released after desorption and respiking. This can be seen in Figs. 33-40. The amount released in general increased with increasing initial loading of the sorbent, e.g. for isotherm points at higher aqueous concentrations. This is expected as not only the initial loading increases along the isotherm but as well the spiked amount of the second compound is higher for these isotherm points.

The released masses after respiking for each combination of sorbent and compound are summarized in Tab. 14, together with the isotherm data for the first sorbed compound (Sorptive 1) and the second sorbed compound (Sorptive 2). The desorbed masses after respiking are reported as the average of all analyzed samples. It can be seen, that especially the charcoal has desorbed masses between 11.2 % of the initially sorbed mass for PCE and 18.1 % for p-Xylene. However, also for the activated carbon substantially amounts desorbed, ranging from 3.6 % for PCE to 7.9 % for p-Xylene. For the microporous Zeolite Y-200 with a rigid pore structure no desorbed mass could be detected, considering a detection limit of about 0.1% of the initially sorbed mass.

Tab. 14: Results of the multi-step batch experiments. (i) Sorption of one compound (Sorptive 1) on a sorbent. (ii) After desorption of Sorptive 1, sorption of a second compound (Sorptiv 2). (iii) Desorbed mass of Sorptive 1, and, (iv), final extraction of the sorbents using Methanol to calculate the total desorbed mass of Sorptive 1 (in % of the initially sorbed mass).

Sorbent	Sorptive 1	log K_{Fr} (L kg^{-1})	n (-)	Sorptive 2	log K_{Fr} (L kg^{-1})	n (-)	Desorbed mass (%) Sorptive 1	Extracted mass (%) Sorptive 1	Total mass (%) Sorptive 1
Act.carbon	PCE	5.04	0.43	TCE	4.65	0.41	3.6	0.3	**3.9**
	TCE	4.85	0.39	PCE	4.95	0.46	5.0	0.4	**5.4**
	o-Xylene	5.02	0.29	p-Xylene	4.62	0.48	7.5	1.1	**8.6**
	p-Xylene	4.91	0.39	o-Xylene	4.87	0.42	7.9	0.1	**8.0**
Charcoal	PCE	4.80	0.26	TCE	4.42	0.39	11.2	0.1	**11.3**
	TCE	4.63	0.29	PCE	4.62	0.29	13.0	1.7	**14.7**
	o-Xylene	4.70	0.22	p-Xylene	4.39	0.49	17.0	2.5	**19.5**
	p-Xylene	4.58	0.28	o-Xylene	4.40	0.27	18.1	3.1	**21.2**
Zeolite	PCE	3.24	1.60	TCE	2.83	1.06	< 0.1	0.2	**0.2**
	TCE	2.75	1.15	PCE	3.32	1.56	< 0.1	0.2	**0.2**
	o-Xylene	3.16	1.43	p-Xylene	3.01	1.31	< 0.1	0.4	**0.2**
	p-Xylene	3.27	1.24	o-Xylene	3.21	1.51	< 0.1	0.4	**0.2**

The amounts of a compound that could be desorbed by a simple respike of a similar compound in a comparably short time period (7 days) are amazingly high, considering the fact that during the preceding regular desorption, that lasted between 4 weeks and three month, the compound could not be detected in the water phase above the detection limit after the final 2 weeks of desorption. This might also indicate, that slow desorption kinetics, which in principal could also explain the observed behavior, is not the dominant process responsible for the occurrence of such a significant desorption resistant fraction.

As a last step, the water phase was withdrawn from the vials and replaced by 5 ml of methanol for final extraction. As indicated in Table 14, especially for the charcoal some more percentages of the initially sorbed mass could be extracted, ranging from 0.1 % for PCE to 3.1 % for p-Xylene. For the activated carbon and the Zeolite Y-200, with only one exception, only less than 0.5 % of the initially sorbed mass could be extracted by the methanol (Table14). This indicates, that already by simple respiking the large majority of desorption resistant fraction could be recovered.

In total, up to 21.2 % of the initially sorbed masses were desorption resistant (charcoal and p-Xylene), i.e. this mass was not desorbing by simple lowering the aqueous phase concentration.

5.4.2 Interpretation of the results

The three sorbents showed large differences with respect to the postulated desorption resistant fraction. The charcoal showed in general largest desorption resistant fractions, ranging from 11.3 % for PCE to 21.2 % for p-Xylene. Also the activated carbon sorbed substantial amounts of sorbent that were not released by a simple desorption lowering the aqueous phase concentration (from 3.9 % for PCE up to 8.0 % for p-Xylene). The zeolite Y-200 showed only minor fractions that were desorbed by respiking and methanol extraction.

The pronounced differences have to be attributed to the different structures of the sorbents. While the zeolite is a rigid, microporous material with well defined pore structure, the charcoal is assumed to have a sheet like structure that is to some extend flexible and can adjust to a sorptive uptake of organic contaminants. The activated carbon is somewhat intermediate in terms of the structure.

The sheet like structure of the charcoal might explain the large fraction of a sorbent that is desorption resistant, a concept introduced by Braida et al. (2003). The material might swell during sorption resulting in a restructuring of the sheets. During desorption, a rearrangement of the sheets might lead to an entrapment of molecules. During a second sorption step, another rearrangement of the charcoal structure may lead to a release of the trapped molecules. This concept is illustrated in Fig. 38.

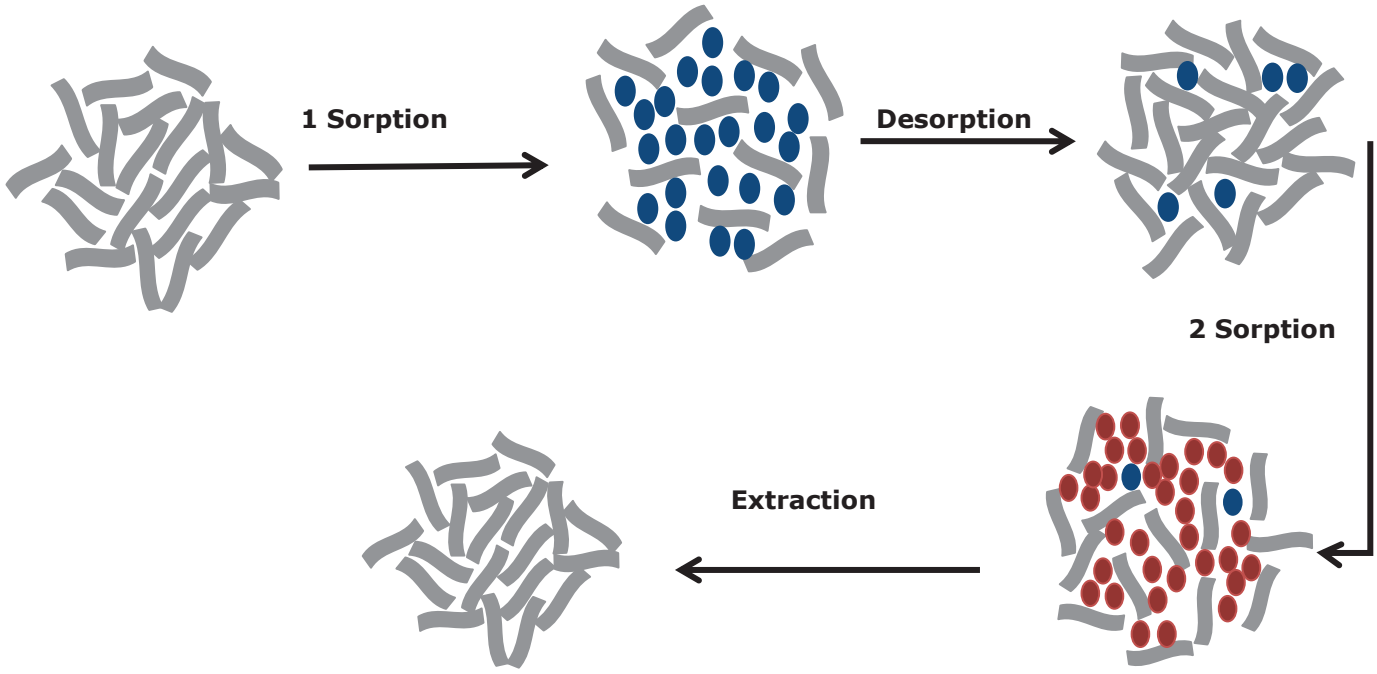


Fig. 38: Conceptual diagram of the proposed mechanism leading to irreversible sorption in the case of charcoal (after Braida 2003)

On the contrary, the Zeolite Y-200 does not show any substantial desorption resistant fraction. This can be attributed to the rigid pore system that allows free diffusion of compound into the system during sorption and out of the system during desorption.

As a second finding it could be shown, that desorbed masses after respiking, indicating the desorption resistant fraction, were substantially higher for the aromatic compounds o-Xylene and p-Xylene compared to the aliphatic compounds TCE and PCE. This might indicate the higher affinity of the aromatic compounds to the carbonaceous materials as these materials are known to contain aromatic structures.

6. SUMMARY

The Freundlich isotherm model can be expressed as a model taking into account partitioning and pore-filling sorption processes. All isotherms are frequently nonlinear displaying Freundlich n values for charcoal and activated carbon. This nonlinearity was observed over three orders of magnitude in concentration and extends to a very dilute solution. In general, the Freundlich model describes the measured data reasonably well - K_f increases with decreasing water solubility. The sorption capacities increase with increasing organic content, based on dual mode model theory and the sorption affinity of contaminates displaying the following trend: activated carbon > charcoal > peat. The linear and nonlinear sorption behavior in different organic matter fractions is attributed to the non-specific hydrophobic partitioning in the amorphous domain and to the site-specific and capacity-limited covalent binding in a condensed domain, respectively. Competitive sorption occurr between corresponding solute pairs, where structurally similar molecules are present. These results are in accordance with the dual mode model of sorption to OM in which both solid-phase dissolution and hole (site)-filling mechanisms take place and in which competition takes place only in the hole-filling domain. As shown, the organic molecules can occupy and block adsorption sites in OM. The results also indicate decreasing capacity efficiency for peat during sorption processes, due to adsorption having occurred in low concentrations. For activated carbon and charcoal, however, the main sorption mechanism is pore-filling.

In multi-step batch sorption-desorption experiments it could be shown, that a significant sorption hysteresis, or an extremely slow release of sorbed organic contaminants, has to be taken into account for carbonaceous sorbents. Especially for the charcoal and aromatic compounds, about 20 % of the initially sorbed compound is not released with significant rates by a simple decrease in the aqueous concentration of the respective compound. A subsequent sorption of another compound on the sorbent can, however, result in a more or less spontaneous release of the initially sorbed compound. This might be due to a displacement of the original compound comparable to a competitive effect. In principle, in the case of the charcoal, also a physical entrapment of molecules due to rearrangement of charcoal sheet-like structure might play a role with respect to the observed effects. However, it has to be taken into account, that desorption resistant fraction was similar at low concentrations compared to high loadings. At low loadings, no significant swelling of the charcoal is assumed.

For the Zeolite Y-200 no indications for desorption resistant fraction was found. It can be assumed, that the rigid and well defined structure of the Zeolite enables a free

access to the internal porosity of the zeolite during sorption as well as during desorption.

In conclusion it can be stated that, at least in these experiments, desorption-resistant fraction cannot be set equal to an ultimate contaminant sink. The resorption of a compound on the sorbent would lead to a contaminant release due to competitive effects. This effect can have significant impacts for the remediation of contaminated sites. First, remediation targets for the solid phase might not be achievable during e.g. a pump-and-treat measure and, secondly, active remediation measures by pumping might lead to a diversion of plumes into areas that have already been remediated, and would lead there to a desorption of the resistant contaminant fraction.

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